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A TEXTBOOK OF THERMODYNAMICS

BY

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PREFACE TO THE FIRST EDITION

THERE are already in existence a number of books on thermodynamics dealing either with the theoretical side of the subject or with the detailed development and applications thereof in some particular direction. There appear to be, however, few books showing the variety of subjects to which thermodynamics can be applied, and it was in the hope of remedying this deficiency that this book was written. As far as possible the aim of comparing theoretical deductions with experimental results has been kept in view in order that those primarily interested in experimental work may, perhaps, appreciate more fully the aid rendered by mathematical physicists.

Although this book is designed principally to cover the course in thermodynamics necessary for an honours degree in physics, it is hoped that it will be of use, not only to students of this subject, but to all who require a general introductory treatise on thermodynamics.

My thanks are due to Dr. R. A. Robinson for reading the major portion of the manuscript, and to Mr. V. H. L. Searle, who read the whole of the proofs and made many valuable suggestions and criticisms.

F. E. HOARE.

EXETER
April 1931.

PREFACE TO THE SECOND EDITION

This edition remains substantially the same as the first, the topics dealt with and the general method of presentation remaining unaltered, although advantage has been taken of the opportunity to revise certain portions of the text where there appeared to be some obscurity or a different presentation seemed advisable. The notation has been altered throughout in accordance with the recommendations made in the recent report presented by the Joint Committee of the Chemical, Faraday and Physical Societies.

Included in this edition is a collection of examples with answers. These have been carefully designed, and it is hoped that a proper balance between examples intended as exercises in the derivation and manipulation of thermodynamical equations and those of a numerical character has been maintained. In the more difficult examples, notes indicating the method of solution have been provided; a student of average ability, well acquainted with the matter in the text, should be able to tackle the majority of the examples satisfactorily.

My thanks are due to the many correspondents who have indicated errors in the previous edition and possible improvements in this. In particular I wish to thank Professors C. H. Berry, W. E. Curtis and G. D. West.

F. E. HOARE.

Exeter,
August, 1938.

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THERMODYNAMICS

CHAPTER 1

GENERAL PRINCIPLES

1. Introductory.—The subject-matter of thermodynamics is the *relation of heat to mechanical energy and the laws which govern* the conversion of one into the other. It is a common fact of everyday experience that heat can be converted into work, as for example in the steam engine, which takes in heat at a high temperature and rejects heat at a lower temperature. The steam engine is typical of a large class of engines known as Heat Engines, which perform work by lowering heat from one temperature level to another, somewhat analogously to the manner in which a waterwheel does work by lowering water from a high to a low level. Without mathematical investigation it is not possible to predict how much of the heat taken in at the higher temperature can theoretically be transformed into work. Naturally the greater the amount that can be so transformed the more economical will be the engine, and from the point of view of practical thermodynamics the object of a heat engine is to get work done with the minimum expenditure of fuel. Heat differs from other forms of energy in that it is not possible to convert it all into work except in one special set of circumstances which cannot be realised practically. These circumstances demand a condenser at the absolute zero of temperature, and for any higher temperature of the condenser only a fraction of the heat supplied can be converted into work, even with a theoretically perfect engine. To the engineer it is of the utmost importance that the laws governing the transformation of heat should be known in order that the most efficient engine may be designed.

Although thermodynamics had its origin in considerations of the efficiency of heat engines, its use at the present day is by no means restricted to this field alone. By theoretical considerations it is possible to predict the variation of physical quantities in certain circumstances and to deduce relations between them of the first importance in experimental work. Also the possibility of chemical reactions and the equilibrium between different substances, as well as a number of related problems, can be investigated by thermodynamics.

The connection between chemical equilibrium and the efficiency of a heat engine might at first seem extremely remote, but as the subject is developed it will be seen that the whole structure of thermodynamics rests upon the foundations of two simple laws, both of which are generalised summaries of experience.

2. Temperature.—Temperature is usually defined as a certain fraction of the difference between two fixed temperatures which are easily and accurately reproducible. For this purpose the melting-point of pure ice and the boiling-point of pure water under standard atmospheric pressure are universally adopted. The method of construction of a liquid in glass thermometer, e.g. the ordinary mercury thermometer, is to choose a fine tube of uniform bore and blow at one end a bulb to contain the liquid whose expansion is to be used as an indication of temperature. The bulb is carefully filled with the liquid by successive heating and cooling, and the other end of the tube sealed so that the thermometer contains only the liquid and its vapour. The instrument is placed in melting ice, and the position reached by the top of the liquid column is carefully marked. Next the thermometer is placed in steam issuing from water boiling under standard atmospheric pressure and the top of the liquid column again marked. The two positions are known as the fixed points. The distance between the marks is divided into a certain number of divisions, 100 if a Centigrade thermometer is being made, and 180 for a Fahrenheit thermometer. Each of these divisions is a degree, and equal intervals of temperature will be defined in this manner by equal amounts of difference between the expansion of the liquid and that of the glass in which it is contained. This introduces arbitrariness into the temperature as measured, for the height to which the liquid rises in the tube will depend upon the liquid chosen for the thermometric substance as well as upon the peculiarities of the glass. It is possible to construct mercury in glass thermometers which, although of uniform bore and agreeing at the fixed points, differ by as much as half a degree for readings in the centre of the scale.

We are not limited to liquids however as thermometric substances. Gases are in general found to have a much more uniform coefficient of expansion than liquids, and are therefore better suited for use as thermometric substances. Gas thermometers can be divided into two classes, depending upon the conditions under which they are used. In constant pressure thermometers the pressure is kept constant by adjustment of a mercury column whilst the volume varies, and in the other class the volume is kept constant by altering the pressure.

Fig. 1 represents a simple form of gas thermometer which can be used either as a constant volume or constant pressure instrument. The gas is contained in the glass bulb A which communicates by a narrow tube with the tube B. The latter is graduated in ccs., and is connected by flexible rubber tubing to a reservoir C which can be raised or lowered at will.

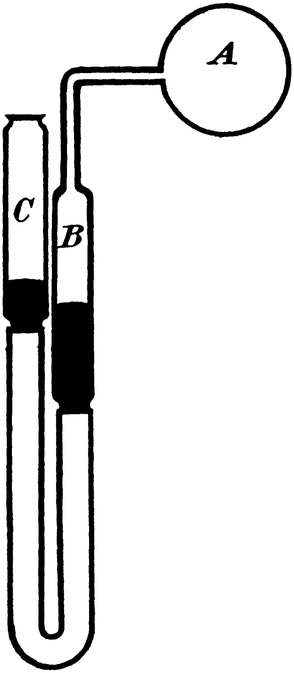

FIG. 1.
Simple Gas Thermometer.

When using the apparatus as a constant volume thermometer the mercury meniscus is adjusted to correspond with a fixed mark on B by raising the reservoir C. The pressure to which the gas is subjected is atmospheric—in cms. of mercury—plus the difference in level of the mercury in B and C.

Let the pressure be p_0 when the bulb is in melting ice and p_1 when surrounded with steam; also let the pressure be p when the bulb is in contact with the body whose temperature we desire to measure.

The Centigrade temperature t_v of the body measured on the constant volume scale with this particular thermometer is then defined as:

$$t_v = \frac{p - p_0}{p_1 - p_0} \times 100.$$

Using the instrument as a constant pressure thermometer the mercury levels in B and C are adjusted to be the same by altering the height of the reservoir C. The change in volume of the gas can be measured by the movement of the mercury in B. A small correction is necessary for the fact that the gas in B is usually not at the same temperature as that in A. As this would complicate our equations we will suppose that A and B are always at the same temperature.

Let v_0 be the volume of the gas at the ice point, v_1 the volume at the steam point, and v the volume at the temperature it is desired to measure.

The Centigrade temperature t_p of the body measured on the constant pressure scale with this particular thermometer is defined as:

$$t_p = \frac{v - v_0}{v_1 - v_0} \times 100.$$

The quantities $\frac{v_1 - v_0}{100\, v_0}$ and $\frac{p_1 - p_0}{100\, p_0}$ are the volume and pressure coefficients respectively of the particular gas and are denoted by α and β. The mean values of α and β for different gases at various initial pressures are given in the following table:

TABLE I.

Gas.	Values of $\alpha \times 10^6$.			Values of $\beta \times 10^6$.		
	$p = 1{,}000$ mm.	760 mm.	500 mm.	$p_0 = 1{,}000$ mm.	760 mm.	500 mm.
Hydrogen.	3660·0	—	—	3662·6	3662·6	3662·3
Nitrogen ·	3673·2	3669·8	3666·8	3673·9	3670·7	3667·9
Air ..	3672·8	3670·8	—	3674·4	—	—
Carbon-dioxide.	3741·0	3723·7	3706·1	3725·6	3712·3	3697·1

It will be seen that a gas at constant pressure expands by an approximately constant fraction of its volume at 0° C. for one degree rise in temperature. Similarly the pressure of a gas at constant volume increases by a certain fraction of its pressure at 0° C. for one degree rise in temperature. If this law were obeyed to the lowest temperatures a point would be reached when the volume of the gas at constant pressure would become equal to zero. This would be at a temperature of $-\frac{1}{\alpha}$ °C., and the pressure of a gas at constant volume would become zero at $-\frac{1}{\beta}$ °C. Denoting $\frac{1}{\alpha}$ by θ_0 and $\frac{1}{\beta}$ by θ_0', we can define new scales of temperatures by the relations:

$$\theta = \frac{v}{v_0}\theta_0, \text{ and } \theta' = \frac{p}{p_0}\theta_0',$$

where the temperatures θ and θ' are measured from new zeros corresponding to $-\frac{1}{\alpha}$ °C. and $-\frac{1}{\beta}$ °C. respectively.

The zero of temperature on the new scales will not only vary from gas to gas, but will not be the same if the thermometer is used as a constant pressure or constant volume instrument. It will be noticed from Table 1, however, that the values of α and β become more nearly equal as the pressure is decreased, and it is found by experiment that as the pressure approaches zero the values become equal and the same for all gases. Consequently by extrapolating the readings of a gas thermometer to zero pressure the readings will be the same for all gases whether used in constant volume or constant-pressure thermometers.* The scale given in this case is the same as the absolute thermodynamic scale.†

3. Unit of Heat.—The unit of heat is defined as the amount of heat required to raise the temperature of unit mass of water by one degree at some particular temperature. The unit of heat depends therefore upon the units of mass and temperature and will vary according to the system of units adopted. In all modern work of a non-technical character the c.g.s. (centimetre, gram, second) system of units is used in conjunction with the Centigrade scale of temperature. The quantity of heat required to raise the temperature of unit mass of water one degree is not the same at all temperatures, and for this reason the initial temperature must be specified. The range 14·5° C. to 15·5° C. is most often adopted, the unit then being the amount of heat required to raise the temperature of one gram of water from 14·5° C. to 15·5° C. This is the 15° C. gram calorie.

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* See Eumorfopoulos, *Proc. Roy. Soc.*, A. **90**, 187 (1914).

† Chapter III.

The mean calorie, which is one-hundredth part of the heat required to raise unit mass of water from the ice point to the steam point, is sometimes employed. This is greater than the 15° C. calorie in the ratio 1·0002 to 1.

Callendar* has suggested that the calorie be defined as one-tenth of the amount of heat necessary to rise the temperature of unit mass of water from 15° C. to 25° C. The reason for this choice is that a range of 10° C. corresponds more closely to the actual experimental procedure in modern calorimetry than a temperature rise of one degree. The mean thermal unit over this range may conveniently be called the calorie at 20° C., although of course it cannot be realised practically except as a mean over a range.

It is sometimes convenient to use the large calorie. This is one-thousand times the calorie as defined above.

The specific heat of a substance is the amount of heat required to raise the temperature of one gram by one degree. The specific heat depends upon the conditions under which it is measured, and these as well as the temperature at which the measurement is made must be specified when dealing with this quantity.

4. Work and Energy.—When a body moves in any direction against an opposing force work is said to be done. The measure of the work done is the product of the opposing force and the displacement. In the c.g.s. system unit work is performed when a force of one dyne is overcome through a distance of one centimetre; this unit is the erg. If a body moves in the direction in which the applied force acts, work is said to be done by the force, whilst if the motion is in the opposite direction work is said to be done against the force. By raising a body from the surface of the earth, for instance, work is done against the force of gravitation, and in falling work is being done by the force of gravitation.

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* Callendar, *Phil. Trans. Roy. Soc.*, A. **199**, 132 (1902).

A body which is capable of performing work is said to possess energy. The value of the energy is measured in terms of the work a body can do and is therefore expressed in the same units as work. The forms in which energy may be manifested are numerous, but two important forms are of constant occurrence and may briefly be described as the energy of motion, kinetic energy, and the energy of position, potential energy. Consider the simple example of a stone being thrown vertically upwards. As the stone leaves the hand it possesses a certain amount of kinetic energy which is equal to the amount of work it can do against gravity in rising to the highest point of its course. When it reaches this point it possesses no velocity but has potential energy equal in magnitude to the kinetic energy it possessed on leaving the hand, provided the effects of air resistance are negligible. Suppose the time of flight of the stone is t seconds and the initial velocity was v cms. per second; then the height to which it ascends is given by:

$$s = vt - \tfrac{1}{2}gt^2,$$

where g is the acceleration due to gravity.

But the work done is mgs, if m is the mass of the stone, and hence:

$$mgs = mg(vt - \tfrac{1}{2}gt^2) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and this is the kinetic energy originally possessed by the body.

The time of flight to maximum height is the time occupied in losing velocity v when there is a retardation of g cms. per second^2. Hence:

$$t = \frac{v}{g} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

By substitution from (2) in (1) we obtain:

$$\text{Kinetic energy} = mgs = \tfrac{1}{2}mv^2.$$

Whilst the body has been moving upwards work of amount mgs has been done against gravity, so that at its maximum height it possesses potential energy of this amount.

Besides kinetic and potential energy there are strain energy, electrical energy, chemical energy, etc., all of which can be expressed in the same units as we have employed.

5. Theories of Heat.—Since early in the seventeenth century there appear to have been two rival theories as to the nature of heat. Lord Bacon declared that heat was a form of motion and, as has been pointed out by Professor Tait,* Newton's third law of motion in its wider interpretation necessitates the equivalence of heat and mechanical energy. The suggestion of Bacon received but little attention until the beginning of the nineteenth century, and up to that time the caloric theory dominated the field of natural philosophy. According to the caloric theory heat is an imponderable fluid, incapable of being created or destroyed, which permeates the interstices of all matter. An increase in the amount of caloric in a body is shown by it getting warmer, and as it cools so it loses caloric. It must be admitted that this theory provided a plausible explanation of the experimental facts so far as they were then known. The expansion of bodies on being heated was attributed to the greater amount of caloric present. The heating of gases or other substances by rapid compression was supposed to be due to some of the caloric originally present being squeezed out and rendered sensible to a thermometer or the touch. An important part of the caloric theory was the doctrine of Latent Heat propounded by Dr. Black in 1760. When ice is contained in a vessel and heat is communicated to it, no change in temperature occurs until the whole of the ice is melted. From this it was inferred that caloric was able to enter into combination with matter and remain latent as it could not be detected by a thermometer. In the same way heat has to be communicated to water which is on the point of boiling to change it into steam; but steam has the same temperature as the boiling water from which it issues, and therefore steam and water only differ in the respect that the former contains a much greater quantity of caloric.

A direct deduction from this theory is that by rubbing two bodies together the capacity for caloric of one or both of them must be decreased, in consequence of which the caloric contained within them, without undergoing any increase, is able to raise them to a higher temperature. This deduction was tested by Rumford† in 1798 by his cannon-boring experiments. He found that a metal had the same capacity for caloric when in a finely divided state as in the form of a solid block. Also he found that the amount of heat obtainable by friction from a limited system appeared to be inexhaustible, and could not therefore be a material substance.

---

* Tait, *Recent Advances in Physical Science*, p. 32 (1876).

† Rumford, *Phil. Trans. Roy. Soc.* (1798).

Certain very early experiments of Davy* are widely quoted as amongst the earliest verifications of the dynamical theory of heat. These experiments consisted of rubbing together blocks of ice, which after some minutes were observed to be wholly melted. A similar experiment was made with wax attached to a metal plate, against which rubbed a clockwork-driven wheel. This apparatus was stood on a piece of ice in which was cut a channel containing water, and all was under an exhausted bell jar. The arrangement was such that if the heat required to melt the wax had passed from the ice to the clockwork the water would have frozen.

It has been pointed out by Andrade† that with all the resources of modern experimental work the first experiment would be very difficult to perform in a manner to give conclusive results, and that the effects observed by Davy were probably due to conduction, whilst the second was so ill designed as to prove nothing.

Although the caloric theory was not finally abandoned until about 1850, the opinion that it was not competent to explain all the experimental facts was steadily growing. The reluctance of many to abandon the theory was due to an essay published in 1824 by Sadi Carnot, entitled *La puissance motrice du feu*, in which the efficiency of a heat engine is considered. By an unhappy mistake it was assumed that the truth of Carnot's reasoning depended upon the caloric theory. It was not until Clausius and Thomson independently realised that this was not true that the caloric theory was definitely abandoned.

Meanwhile Joule, convinced that heat and work were mutually convertible, had been performing a series of elaborate experiments to discover the exact amount of heat produced by the expenditure of a known amount of work.

6. Joule's Experiments.—In the first series of experiments performed by Joule falling weights were arranged to churn water in a calorimeter, the mechanical energy lost by the weights being taken as equivalent to the heat developed in the water. The arrangement of the apparatus will be seen from Fig. 2. Each of two weights, AA, was secured by strings wound on the axle of a wheel and axle BB; from the wheels strings passed horizontally to a drum D attached to a spindle S carrying brass paddles which revolved in a copper calorimeter C containing a known amount of water. The drum could be detached from the spindle by withdrawing the pin P, so that the weights could be wound up to a height of five feet from the floor without rotating the paddles. By attaching the drum to the spindle the paddles were caused to rotate by the falling weights. Any continuous circulation of the water was prevented by fixed brass vanes attached to the calorimeter. Precautions were taken to make the heat losses small and the effects of radiation and friction in the pulleys were determined by subsidiary experiments and allowed for in computing the final result. Other small corrections, such as that for the residual velocity of the weights on reaching the floor, were also made.

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* Davy, *Complete Works*, vol. ii, p. 11.

† Andrade, *Nature*, **135**, 359 (1935).

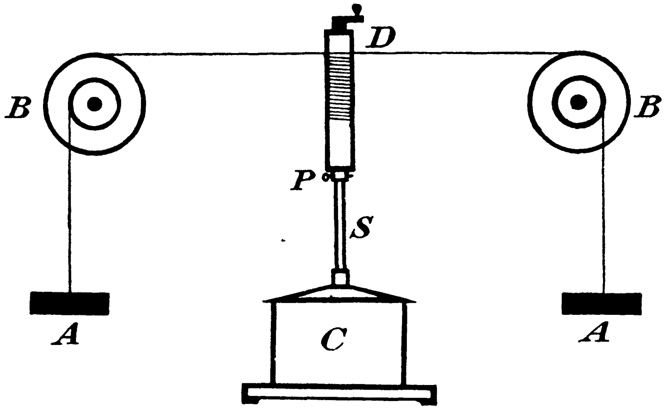

FIG. 2.

Joule's Apparatus for Determining the Mechanical Equivalent of Heat.

In an experiment the weights were wound up and allowed to fall twenty times. Knowing the rise in temperature, which was measured on a sensitive mercury thermometer, and the heat capacity of the calorimeter and contents, the total heat generated could be determined and the "mechanical equivalent of heat" deduced.

Several other methods, such as churning mercury instead of water, and developing heat, not by fluid friction, but by means of a bevelled cast-iron ring rubbing against another bevelled iron ring in mercury, were employed by Joule, but they all gave approximately the same result.

Since Joule a number of physicists have made determinations of the mechanical equivalent of heat. Some of these have been by direct methods, but a large number have been electrical. As water has been used as the calorimetric substance in the majority of experiments these can be considered as methods of finding the mechanical equivalent or the variation of the specific heat of water with temperature. The following table gives the values found by various observers.*

TABLE II.

	Mechanical Equivalent. Ergs per 20 °C. Calorie.
Direct determinations:	
Joule	$4 \cdot 1680 \times 10^7$
Rowland	$4 \cdot 1822 \times 10^7$
Reynolds and Moorby	$4 \cdot 1758 \times 10^7$
Laby and Hercus	$4 \cdot 1809 \times 10^7$
Indirect electrical determinations:	
Griffiths	$4 \cdot 1904 \times 10^7$
Schuster and Gannon	$4 \cdot 1898 \times 10^7$
Callendar and Barnes	$4 \cdot 1795 \times 10^7$
Bousfield and Bousfield	$4 \cdot 1767 \times 10^7$
Jaeger and Steinwehr	$4 \cdot 1821 \times 10^7$

7. Properties of Gases.—In considering gas thermometers we have seen that a new scale of temperature can be defined by either form of thermometer, and the scales are approximately the same. If θ is the temperature on the gas scale we can therefore write:

$$pv = R\theta \quad \ldots\ldots\ldots \quad (3)$$

where the equation refers to unit mass of gas and R is a constant for a particular gas, but has different values for different gases.

Equation (3) is a summary of the laws of Boyle and Charles.

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* See Laby, *Proc. Phys. Soc.*, **38**, 169 (1926), and *Phil. Trans. Roy. Soc.*, A. **227**, 63 (1928).

Boyle found that the product of pressure and volume for a given mass of gas at constant temperature was constant, and Charles's law may be expressed by saying a gas at constant pressure expands by $\frac{1}{273}$ of its volume at 0° C. for each degree Centigrade rise in temperature. We may expect then that the absolute zero is at approximately $-273°$ C. The value as deduced from the most accurate experimental data is about $-273 \cdot 18°$ C.*

No known gas obeys equation (3) under all conditions, but the relation may be regarded as a very good approximation to the behaviour of all gases which are sufficiently removed from the conditions causing liquefaction. A very useful concept is that of a perfect gas for which the equation would be true for all conditions of pressure and temperature. Such a gas would be invaluable in experimental physics, for by using it in a thermometer the temperature scale would be definitely fixed. It will be shown in Chapter IV that the scale of temperature defined by a perfect gas corresponds to Kelvin's Absolute Scale, which is independent of the properties of any particular substance.

8. Experiments of Andrews and Amagat.—It will be seen that for a gas which obeys equation (3) the pressure plotted against volume at constant temperature will give a rectangular hyperbola, the axes of p and v being the asymptotes. Andrews in 1863 made a series of experiments with carbon dioxide, in which the pressure on the gas contained in a glass tube was gradually increased, the volume corresponding to each value of the pressure being noted. For any one series the temperature was constant so that the curves obtained by plotting p against v are isothermals. Fig. 3 shows the general form of the isothermals of carbon dioxide.

If the temperature was sufficiently high it was found that the isothermals approximated in form to a rectangular hyperbola, but as the temperature was lowered the deviation from the form for a perfect gas became more noticeable. For a particular isothermal, $30 \cdot 9°$ C., a portion of the curve became horizontal, and for all the isothermals below this there were two sudden discontinuities in the curve, between which the volume decreased without any increase in pressure. The horizontal portion of the curve corresponds to liquefaction. At temperatures above $30 \cdot 9°$ C. it was found to be impossible to liquefy the gas however great the pressure, and for this reason 30·9° C. is called the critical temperature of carbon dioxide, and the isothermal for this temperature the critical isothermal.

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* See Chapter V.

At the point A, Fig. 3, the substance would undoubtedly be regarded as being in the gaseous state and at B in the liquid state. By moving from A parallel to the pressure axis until an isothermal above the critical isothermal is reached, i.e. by heating the gas at constant volume, moving along this isothermal until a point horizontally opposite B is reached, and then cooling the gas at constant pressure the change from gaseous to liquid state can be made without any sudden discontinuity in the state of the substance occurring. This is spoken of as the continuity of the liquid and gaseous states.

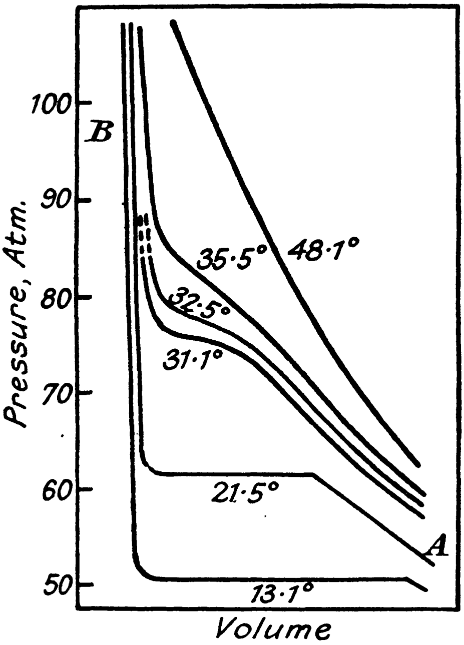

FIG. 3.
Isothermals for Carbon Dioxide.

The deviations from Boyle's law have been investigated in a different manner by Amagat and other observers. The experiments of Amagat are typical and were the first where such large pressures were employed.

In these experiments the gas under examination was enclosed in a tube and subjected to the pressure of a column of mercury. Amagat worked at the bottom of a mine shaft and had a tube 327 metres long extending up the shaft to contain the mercury and produce pressures up to 430 atmospheres. In representing the results the product pv was plotted against p. Figs. 4, 5, and 6 show the form of the curves for nitrogen, hydrogen, and carbon dioxide respectively.

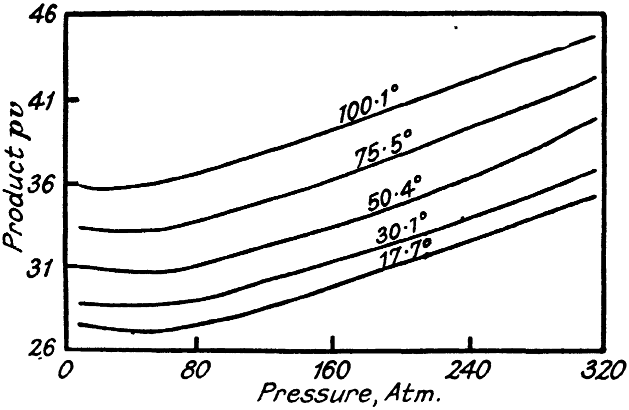

FIG. 4.

Amagat Isothermals for Nitrogen.

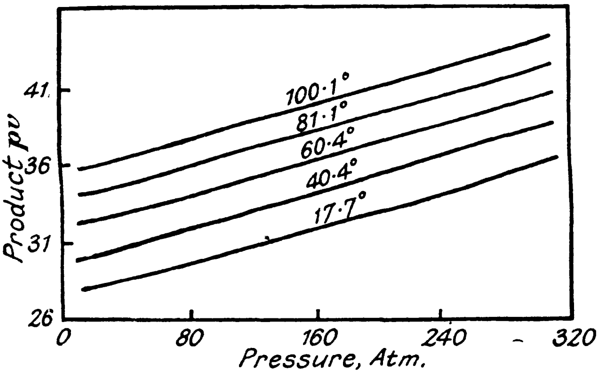

FIG. 5.

Amagat Isothermals for Hydrogen.

It will be noticed that for nitrogen and carbon dioxide the curves first descend, reach a minimum, and then ascend, whereas the curves for hydrogen ascend along their whole length. A gas which obeyed Boyle's law under all conditions would of course give a straight line parallel to the pressure axis at each temperature. The reason for hydrogen behaving differently from other gases was somewhat obscure at the time of Amagat's experiments, but extended researches by Witkowski * have shown that at low temperatures hydrogen exhibits the same characteristics as other gases.

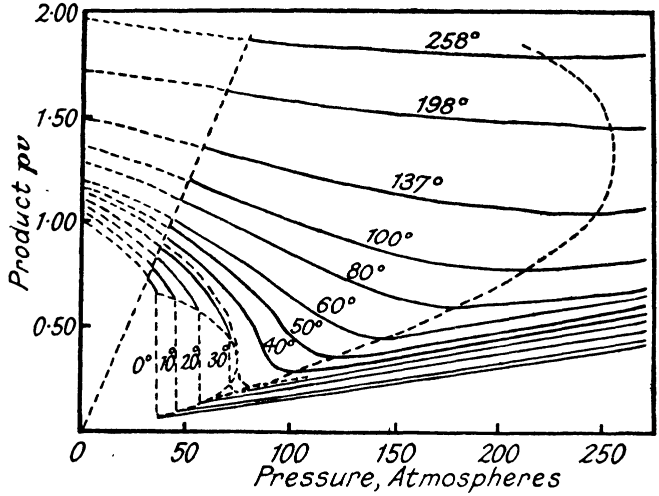

FIG. 6.

Amagat Isothermals for Carbon Dioxide.

We will return to the explanation of these results in Chapter VI.

The case of carbon dioxide, Fig. 6, is interesting. The minimum points on the isothermals advance to the right as the temperature rises, but this advancement ceases at high temperatures and a retrograde motion supersedes, giving a parabolic form to the locus of minima. At temperatures in the neighbourhood of the critical temperature the dip becomes increasingly pronounced, and at temperatures below this, part of the curve is vertical corresponding to liquefaction.

9. Mathematical Notes.—In the subsequent work much use will be made of the differential calculus and some important theorems on partial differentiation will be used continually. As a clear understanding of the physical interpretation of these is necessary a brief review of the subject is given here.

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* Witkowski, *Bull. de l'Acad. de Sc. de Cracovie* (1905).

Suppose it be given that y is some function of the variable x and is continuous over a certain definite range of x. Let δx be any increment of the variable x and δy the corresponding increment of y, such that $y + \delta y$ lies within the range of y continuous. Then the value of the ratio $\frac{\delta y}{\delta x}$ as δx tends to zero is the differential coefficient of the function y with respect to x and is written $\frac{dy}{dx}$.

If x is a function of the two variables y and z such that it can be written:

$$x = f(y, z), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

there are two differential coefficients of the function. In the first case it might be differentiated with respect to y keeping z constant, and in the second with respect to z keeping y constant. These differential coefficients are known as partial differential coefficients, and are written:

$$\left(\frac{dx}{dy}\right)_z = \left(\frac{df}{dy}\right)_z \quad \text{and} \quad \left(\frac{dx}{dz}\right)_y = \left(\frac{df}{dz}\right)_y,$$

where the suffix outside the bracket denotes the variable kept constant for the differentiation.

If it is required to find the variation in the quantity x, given by equation (4), when y and z are increased by the amounts δy and δz it may be done by an extension or double application of Taylor's theorem.

For a function of a single variable such as

$$x = f(y)$$

we have by Taylor's theorem

$$\begin{aligned} x + \delta x &= f(y + \delta y) \\ &= f(y) + \delta y \cdot \frac{df}{dy} + \frac{\delta y^2}{2!} \cdot \frac{d^2 f}{dy^2} + \ldots \end{aligned}$$

When x is a function of the two variables y and z the value of the function $f(y + \delta y, z + \delta z)$ is found by first considering the second variable constant at the value $z + \delta z$ and expanding in terms of y and δy only by Taylor's theorem. It will be convenient to represent the partial derivative of the function $f(y, z)$ with respect to y by f_y etc. Consequently on expansion we have

$$\begin{aligned} x + \delta x &= f(y + \delta y, z + \delta z) \\ &= f(y, z + \delta z) + \delta y \,.\, f_y(y, z + \delta z) \\ &\quad + \tfrac{1}{2} \,.\, \delta y^2 \,.\, f_{yy}(y, z + \delta z) + \text{higher terms in } \delta y. \end{aligned}$$

Using Taylor's theorem again to expand each of the terms on the right-hand side of this equation we have:

$$\begin{aligned} x + \delta x = f(y, z) &+ \delta y \,.\, f_y(y, z) + \delta z \,.\, f_z(y, z) \\ &+ \tfrac{1}{2}\Big\{(\delta y^2 \,.\, f_{yy}(y, z) + 2\delta y \,.\, \delta z \,.\, f_{yz}(y, z) + \delta z^2 \,.\, f_{zz}(y, z)\Big\} \\ &+ \text{higher terms in } \delta y \text{ and } \delta z, \quad \ldots\ldots\ldots \quad (5) \end{aligned}$$

or finally:

$$\delta x = \left(\frac{dx}{dy}\right)_z \delta y + \left(\frac{dx}{dy}\right)_y \delta z + \text{higher terms.}$$

If the variations δy and δz are continuously decreased in magnitude, the terms involving powers of the variations higher than the first will become vanishingly small, and we may then write:

$$dx = \left(\frac{dx}{dy}\right)_z dy + \left(\frac{dx}{dz}\right)_y dz \quad \ldots\ldots \quad (6)$$

where the symbol d signifies an infinitesimal variation.

If instead of expanding the function $f(y + \delta y, z + \delta z)$ in terms of δy initially the expansion had been made first in terms of δz a similar equation to (5) would have resulted, except that a term involving $f_{zy}(y, z)$ instead of $f_{yz}(y, z)$ would have been obtained. Since the two forms must obviously be the same it follows that

$$f_{yz}(y, z) = f_{zy}(y, z)$$

or

$$\frac{d^2x}{dydz} = \frac{d^2x}{dzdy} \quad \ldots\ldots\ldots \quad (7)$$

That is, the order in which the differentiations are performed is immaterial.

Let us now consider an equation of the type

$$dx = Mdy + Ndz \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If this equation is obtainable from an equation such as (4) it will be seen by comparison with equation (6) that M and N must be of the form

$$M = \left(\frac{dx}{dy}\right)_z, \quad N = \left(\frac{dx}{dz}\right)_y.$$

Conversely if M and N are of this form there exists a functional relation such as equation (4) connecting the variables. A test as to the existence of such a relation is provided by equation (7); *i.e.*, if

$$\frac{dM}{dz} = \frac{dN}{dy} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

x, y and z are connected by a relation such as equation (4).

When this is so dx is referred to as a complete or perfect differential. The physical meaning of this is simply that the change in x in any transformation depends only upon the initial and final values of the variables y and z, for if the initial and final values of these variables are y_0, z_0 and y_1, z_1 the change in x may be written

$$\Delta x = x_1 - x_0 = f(y_1, z_1) - f(y_0, z_0).$$

In other words, the change in the dependent variable x is independent of the path — in space if x, y, z are regarded as Cartesian coordinates of a point — adopted for the transformation.

It often happens, however, that an equation of the type (8) occurs without (9) being satisfied. In this case there will be no functional relationship of the form (4) existing between the variables x, y, z, and the change in the value of x will not depend upon the initial and final values of y and z only, but upon the path adopted to effect the transformation.

As a simple example of frequent occurrence in thermodynamics let us suppose

$$N = \mu y.$$

where μ is a constant and M is constantly zero. The condition of equation (9) is obviously not satisfied in this case. As M is always zero this imposes a restriction to a particular path which may be supposed represented by the curve AB, Fig. 7. The change in x in going from A to B will now be given by:

$$\Delta x = \sum_{A}^{B} \mu y dz,$$

which is μ times the area bounded by the curve, the z axis and the lines AN, BM, and depends upon the shape of the curve as well as upon the positions of the points A and B.

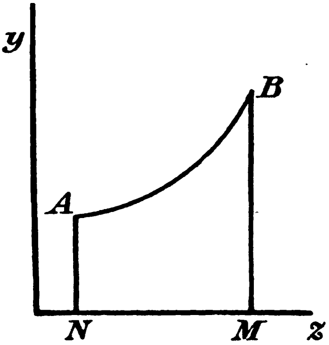

FIG. 7.

When the variable x is such as to possess no complete differential it will be convenient to distinguish a small variation in its magnitude from that of some other variable possessing a complete differential. This will be done in what follows by using the symbols dx and δx to represent infinitesimal variations which are and are not complete differentials respectively.

Returning to equation (6), suppose z to be kept constant—*i.e.*, $dz = 0$. On division by dx we have:

$$1 = \left(\frac{dx}{dy}\right)_z \cdot \left(\frac{dy}{dx}\right)_z$$

or

$$\left(\frac{dx}{dy}\right)_z = 1 \bigg/ \left(\frac{dy}{dx}\right)_z,$$

which shows that the reciprocal of a partial differential coefficient is the same as the inverted coefficient.

Again, in equation (6), keeping x constant—*i.e.*, $dx = 0$—we have on division by dy:

$$0 = \left(\frac{dx}{dy}\right)_z + \left(\frac{dx}{dz}\right)_y \cdot \left(\frac{dz}{dy}\right)_x,$$

or, using the previous result,

$$\left(\frac{dx}{dy}\right)_z \cdot \left(\frac{dz}{dx}\right)_y \cdot \left(\frac{dy}{dz}\right)_x = -1. \quad . \quad . \quad . \quad . \quad (10)$$

CHAPTER II

THE FIRST LAW OF THERMODYNAMICS

10. The Conservation of Energy.—In mechanics the principle of conservation of energy is of general application, but knowing nothing of the phenomena of heat it would be a difficult matter to decide in all cases what becomes of the energy associated with a system. When a block of wood, for instance, is projected across the surface of a plane table there is initially a definite amount of kinetic energy possessed by the block. After a time, provided that the initial velocity is not sufficient to carry the block right off the table, it is brought to rest by the frictional forces between the two surfaces. When this occurs the kinetic energy of the block is zero, but by the principle of conservation of energy, the energy which has apparently disappeared cannot have been destroyed. It is well known, of course, that the effect of frictional forces is to generate heat, as in a mechanical bearing which is not well lubricated, and we have already seen that there is a direct proportionality between work done and heat generated. Consequently, the principle of conservation of energy can be extended to include the energy of heat. The principle so extended is the first law of thermodynamics.

The proportionality between work done and heat generated may be expressed mathematically by the equation:

$$W = Jq, \qquad \ldots \ldots \qquad (11)$$

where W is the mechanical energy, q the heat energy, and J the mechanical equivalent of heat, the magnitude of which depends upon the system of units adopted. There is nothing in this equation to indicate that a given quantity of heat cannot be wholly converted into mechanical energy. We shall consider in the next chapter the restrictions imposed upon the conversion of heat into work, but it must be remembered that work can be completely transformed into heat. Equation (11) may be regarded as a mathematical expression of the first law of thermodynamics, although not the most general one.

11. Internal Energy.—Consider the way in which heat communicated to a body may be used. If the heat is absorbed without the performance of external work it all goes to increase the store of energy within the substance. This store of energy is the internal energy. A body in a given state has internal energy associated with the configuration and motion of its molecules, and any change in internal energy between two different states of the body depends only upon the initial and final states, and in no way upon the process by which the change is effected. There are no experimental methods for measuring the internal energy in a given state, but changes are readily measured; consequently, if a certain definite state of the body is decided upon as that from which changes of internal energy are to be measured, this quantity can always be expressed as an excess over that in the arbitrarily chosen state.

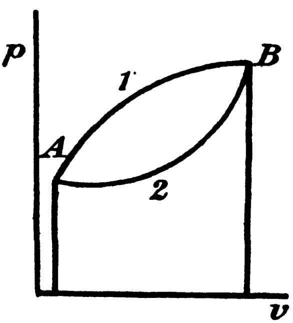

FIG. 8.

If a body takes in heat and does external work at the same time, the heat absorbed must be equivalent to the external work done together with the change in internal energy. Suppose the initial condition of the body is represented by the point A on the p — v diagram, Fig. 8. Let it be transformed to the state B by the path 1. The heat absorbed in passing from A to B, q_1, is given by:

$$q_1 = E_B - E_A + W_1 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where E_A and E_B are the internal energies in the states A and B and W_1 the external work done, all the quantities being expressed in work units. Equation (12) may be regarded as a general statement of the first law of thermodynamics.

If now the body is made to return to its original state by a different path the heat absorbed and the external work will, in general, be different from their former values. Thus the heat absorbed in passing from B to A by the path 2 is given by:

$$q_2 = E_A - E_B + W_2. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Adding equations (12) and (13):

$$q_1 + q_2 = W_1 + W_2.$$

The interpretation of this is that in any process by which a body goes through a series of changes and returns to its original condition the sum of the heat absorbed is equal to the total external work performed. Such a process is known as a cyclic process. In calculating the sum $q_1 + q_2$ heat given to the body is reckoned positive and heat taken away negative. Similarly work done by the body is positive and work done on it negative. Hence $q_1 + q_2$ is the amount of heat which disappears in the cycle and $W_1 + W_2$ the net external work done.

For an infinitesimal process equation (12) may be written in the form:

$$\delta q = dE + \delta W. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where δq and δW represent the very small amounts of heat absorbed and work done by the body respectively and dE the change in internal energy. From the foregoing discussion in this section it is clear that the change in internal energy in any process depends only upon the initial and final conditions of the body, whereas the heat absorbed and the external work done depend also upon the path adopted to effect the change. In other words, the internal energy possesses a complete differential, but the heat absorbed and the work done do not. This is expressed in equation (14) by the use of different symbols for a small variation in the two cases.

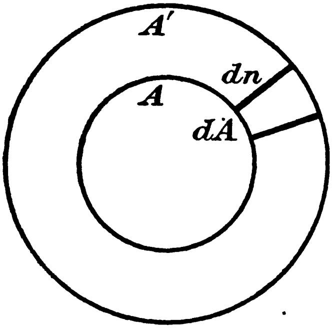

FIG. 9.

12. Work done by Expanding Fluid.

—The work done by a fluid on expansion can be obtained by simple considerations. Let A and A', Fig. 9, represent the surface of a fluid before and after a small expansion against a uniform external pressure p. If the expansion is made extremely slowly no energy of motion will be developed, and the only work done will be in enlarging the volume.

Consider an element dA of the surface and let its displacement along the normal be *dn*. Then the work done by the fluid is given by:

$$\begin{aligned}\delta W &= \Sigma(p\,.\,dA)\,dn,\\ &= p\Sigma dA\,.\,dn,\\ &= p \times \text{increase in volume},\\ &= pdv.\end{aligned}$$

Referring again to Fig. 8 it will be seen that the work done by the substance in expanding from A to B by the path 1 is:

$$W = \sum_{A}^{B} pdv \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

which is the area contained between the curve 1 and the axis of volumes. The work done on the substance in returning from B to A by the path 2 is the area contained between this curve and the axis of volumes. The net amount of work which the substance does during the cycle is equal to the difference between these areas; that is, the area of the cycle represents the work done during the complete cyclic operation.

If the cycle were performed in the reverse direction the area of the closed curve would represent the work expended upon the substance in the cycle.

This method of representing the work done during a cycle is due to James Watt, who invented an instrument called the *Indicator*, by means of which an engine can automatically draw a diagram representing pressure changes in relation to volume changes. Such a diagram, for an actual machine, is accordingly called an *Indicator Diagram*, but should be distinguished from the pressure-volume diagram, which, unlike an indicator diagram, relates to a constant mass of substance.

13. Internal Energy of a Gas.—In a gas the molecules possess potential energy due to the attractive forces between the individual molecules. When the gas expands the average distance between the molecules is increased, and therefore there is an increase in the potential energy. If the gas is made to expand in such a manner that no external work is done and no heat is supplied from outside, the increase in potential energy must take place at the expense of the kinetic energy. Now the temperature of a gas depends upon the average kinetic energy of the molecules, in fact temperature is actually a measurement of this energy. Hence if an increase in potential energy occurs the temperature of the gas would fall.

Experiments were made by Joule to determine the magnitude of this effect with the apparatus shown in Fig. 10. Two receivers, A and B, connected by a tube furnished with a stopcock, were immersed in a bath of water which served as a calorimeter. One of the receivers was exhausted and the other filled with dry air under a pressure of approximately 22 atmospheres. The temperature of the water in the containing vessel was taken by a sensitive mercury in glass thermometer reading to $\frac{1}{200}$ °F. The stopcock was then opened and air allowed to flow from one receiver to the other until equilibrium was established. The water in the bath was then well stirred and its temperature again taken. It was found that no appreciable change had occurred. Joule concluded from this experiment that there is no change in temperature when air is allowed to expand in such a manner that no external work is done. A change of temperature would have

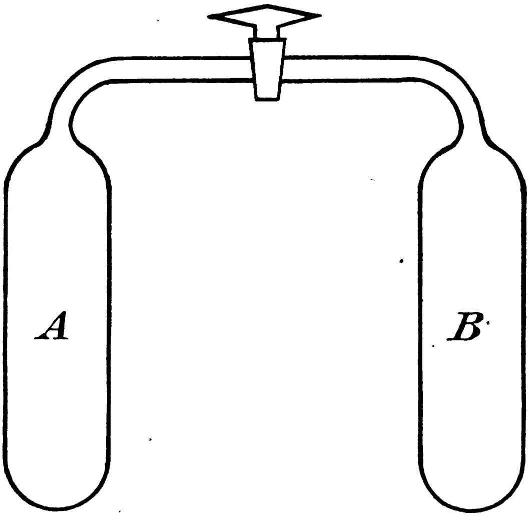

FIG. 10.
Joule's Apparatus.

indicated a change in the potential energy, i.e. a change in the internal energy of the gas, but the absence of any thermal effect shows that the internal energy is independent of the volume. The conclusion follows that the internal energy of a gas is a function of the temperature only, and not dependent upon its pressure or volume. This is known as Mayer's hypothesis.

Joule's experiments were not delicate enough to detect the small change in temperature which is now known to occur in real gases. For the imaginary perfect gas, however, the internal energy depends only upon the temperature. Later, in collaboration with Thomson, an experiment of much greater delicacy, in which the Joule effect plus the effect of departure from Boyle's law was measured, indicated how the internal energy of real gases depends upon the volume.

14. Specific Heats of a Perfect Gas.—Let us now consider the application of the first law of thermodynamics to unit mass of a perfect gas.

When a gas expands, all the external work done is due to volume changes, and the first law for unit mass becomes:

$$\delta q = dE + p dv, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where all the quantities are expressed in work units. Now the change in the internal energy, dE, can be expressed in terms of the changes in volume and temperature. That is:

$$dE = \left(\frac{dE}{dv}\right)_\theta dv + \left(\frac{dE}{d\theta}\right)_v d\theta.$$

But we have seen that for a perfect gas the internal energy is independent of the volume, and therefore $\left(\frac{dE}{dv}\right)_\theta$ is zero.

Hence equation (16) becomes:

$$\delta q = \left(\frac{dE}{d\theta}\right)_v d\theta + p dv \quad . \quad . \quad . \quad . \quad (17)$$

If the volume is kept constant, dv is zero, so putting $dv = 0$ in (17), and dividing each side by $d\theta$, we have:

$$\left(\frac{\delta q}{d\theta}\right)_v = \left(\frac{dE}{d\theta}\right)_v.$$

The term on the left-hand side of this equation is the specific heat at constant volume, c_v, so

$$c_v = \left(\frac{dE}{d\theta}\right)_v,$$

or the rate of variation of internal energy with temperature at constant volume is the same as the specific heat of the substance at constant volume. Hence the first law of thermodynamics for a perfect gas reduces to

$$\delta q = c_v\, d\theta + pdv. \tag{18}$$

For a perfect gas we have the relation:

$$pv = R\theta,$$

or differentiating each side:

$$pdv + vdp = Rd\theta. \tag{19}$$

Substituting from equation (19) for pdv in equation (18) this becomes:

$$\delta q = (c_v + R)d\theta - vdp. \tag{20}$$

If the pressure is constant, dp is zero. Proceeding as before, we have

$$\left(\frac{\delta q}{d\theta}\right)_p = c_p = c_v + R,$$

or

$$c_p - c_v = R. \; . \checkmark \tag{21}$$

That is, the difference in the specific heats of a perfect gas at constant pressure and constant volume respectively is equal to the gas constant.

Combining equations (20) and (21) the first law of thermodynamics for a perfect gas may now be written in the equivalent forms:

$$\left.\begin{aligned} \delta q &= c_v \,.\, d\theta + pdv \\ &= c_p \,.\, d\theta - vdp \end{aligned}\right\} \tag{22}$$

When the conditions of a body are allowed to change in such a manner that no heat enters or leaves it, the transformation is said to be adiabatic. The condition for such a change is obviously

$$\delta q = 0.$$

For an adiabatic change in a perfect gas we have, therefore, from the equations (22):

$$c_p d\theta = vdp,$$

and

$$c_v d\theta = -pdv,$$

or

$$\frac{c_p}{c_v} = -\frac{vdp}{pdv}.$$

Writing γ for the ratio of the specific heats we obtain the equation:

$$\gamma\frac{dv}{v} = -\frac{dp}{p},$$

which on integration, assuming γ constant, gives:

$$pv^\gamma = \text{constant}, \quad . \quad . \quad . \quad . \quad . \quad (23)$$

as the equation connecting pressure and volume for adiabatic changes of a perfect gas. In other words, equation (23) is the equation to an adiabatic line on a p—v diagram.

Combining equations (23) and (3) the relation between pressure and temperature or volume and temperature in adiabatic change is obtained. Thus, from (3):

$$v = \frac{R\theta}{p},$$

which on substitution in (23) gives:

$$\frac{\theta}{p^{\frac{\gamma-1}{\gamma}}} = \text{constant}. \quad . \quad . \quad . \quad . \quad . \quad (23a)$$

Similarly:

$$p = \frac{R\theta}{v},$$

which on substitution in (23) gives:

$$\theta v^{\gamma-1} = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad (23b)$$

15. Ratio of the Specific Heats of Gases.—The ratio of the specific heats of a gas is not the same for all gases, but depends upon the complexity of the molecules. We shall now deduce a relation connecting the ratio of the specific heats and the number of degrees of freedom of the molecule.

It can be shown* that for a gas whose molecules act as small rigid spheres the relation between the pressure and volume is:

$$pv = \tfrac{1}{3}\overline{V^2},$$

where $\overline{V^2}$ is the mean square velocity of translation of the molecules. This can be written:

$$p = \tfrac{1}{3}\rho\overline{V^2},$$

where ρ is the density of the gas.

For a perfect gas we have:

$$pv = R\theta,$$

so the energy of translation of unit mass of gas is given by:

$$\tfrac{1}{2}\overline{V^2} = \tfrac{3}{2}R\theta.$$

If the temperature of the gas is raised by 1° C. the energy of translation of the molecules increases by $\frac{3}{2}R$, and the total energy of the molecules by C_v. Hence we have the relation:

$$\frac{\text{Increase of energy of translation of molecules}}{\text{Increase of total energy of molecules}} = \frac{3}{2}\frac{R}{c_v}. \quad . \quad (24)$$

It has been shown by Maxwell and others that if the molecules of a gas obey the ordinary laws of mechanics there must be the same amount of energy associated with each degree of freedom. This is the principle of the equipartition of energy.

With the motion of translation of a material particle there are associated three degrees of freedom. Let us suppose that the total number of degrees of freedom possessed by a molecule is n. Then using the principle of equipartition of energy we see that

$$\frac{\text{Increase of energy of translation of molecules}}{\text{Increase of total energy of molecules}} = \frac{3}{n},$$

and by comparison with equation (24) we obtain:

$$\frac{3}{2}\frac{R}{c_v} = \frac{3}{n}.$$

---

* Chapter VI.

For a perfect gas $c_p - c_v = R$, and therefore

$$\gamma = 1 + \frac{2}{n}$$

We are now able to calculate the theoretical value for the ratio of the specific heats of various gases. For a monatomic molecule the degrees of freedom are three; a diatomic molecule five; a polyatomic molecule not less than six, rotation of the molecules being neglected in each case. Hence the theoretical values of γ for these molecules are 1·667, 1·400, and not greater than 1·333 respectively. The following table shows the agreement between the theoretical and experimental values.*

TABLE III.

Gas.	Atoms in Molecule.	γ.	
		Experimental.	Theoretical.
Argon	1	1·666	1·667
Helium	1	1·666	
Air	2	1·403	1·400
Carbon monoxide	2	1·404	
Chlorine	2	1·355	
Hydrogen	2	1·408	
Hydrochloric acid	2	1·40	
Nitrogen	2	1·405	
Nitric oxide	2	1·40	
Oxygen	2	1·396	
Carbon dioxide	3	1·302	Not greater than 1·333
Carbon disulphide	3	1·235	
Nitrous oxide	3	1·300	
Sulphur dioxide	3	1·285	
Sulphuretted hydrogen	3	1·340	
Acetylene	4	1·280	
Methane	5	1·310	
Ethylene	6	1·250	
Ethane	8	1·220	

16. Work in Isothermal and Adiabatic Expansion.—The most common types of expansion with which we have to deal in thermodynamics are either isothermal or adiabatic. Having found the equations to an isothermal and an adiabatic line on the p—v diagram, it is possible to calculate the work done in either type of expansion by evaluating the summation of equation (15).

---

* Experimental values from Partington and Shilling, *The Specific Heats of Gases*, p. 201.

(i) *Isothermal Expansion.*—Let the initial volume of a perfect gas be v_1, and the final volume after an isothermal expansion be v_2. Then the work done is:

$$W = \sum_{v_1}^{v_2} p dv = R\theta \int_{v_1}^{v_2} \frac{dv}{v} = R\theta \log \frac{v_2}{v_1}, \quad . \quad . \quad . \quad (25)$$

by substitution for p from equation (3) and integration.

By the first law of thermodynamics the work done must be the same as the heat absorbed less the change in internal energy. Now as we have seen the internal energy of a perfect gas depends only upon the temperature, and therefore equation (25) gives the amount of heat which must be absorbed by a perfect gas in expanding from volume v_1 to v_2 in order to keep its temperature constant.

(ii) *Adiabatic Expansion.*—Equation (23) for an adiabatic change can be written:

$$p_1 v_1^\gamma = p v^\gamma = p_2 v_2^\gamma,$$

where the suffixes 1 and 2 denote the initial and final conditions respectively, and the unsuffixed letters any intermediate state. Hence the work done in an adiabatic expansion is given by:

$$W = \sum_{v_1}^{v_2} p dv = p_1 v_1^\gamma \int_{v_1}^{v_2} \frac{dv}{v^\gamma} = \frac{p_1 v_1 - p_2 v_2}{\gamma - 1}$$

17. Elasticities of a Perfect Gas.—All matter possesses volume elasticity which is defined as the ratio of the stress, or force per unit area, to the strain, or change in volume per unit volume. Denoting the elasticity by K it is given by:

$$K = -v\left(\frac{dp}{dv}\right),$$

the negative sign arising from the fact that elasticities are always expressed as positive quantities.

The value of $\left(\frac{dp}{dv}\right)$ will depend upon the conditions under which the measurement is made, and will in general be different in an isothermal change from that in an adiabatic change. Let the isothermal and adiabatic elasticities be denoted by K_θ and K_q respectively. That is:

$$K_\theta = -v\left(\frac{dp}{dv}\right)_\theta, \text{ and } K_q = -v\left(\frac{dp}{dv}\right)_q.$$

Since we have already seen the form of the connection between the pressure and volume, both for isothermal and adiabatic changes, in the case of a perfect gas, we have on differentiation of equations (23) and (3):

$$\left(\frac{dp}{dv}\right)_q = -\gamma\frac{p}{v} \text{ and } \left(\frac{dp}{dv}\right)_\theta = -\frac{p}{v},$$

and hence

$$\frac{K_q}{K_\theta} = \gamma$$

We have in the above only shown that the ratio of the adiabatic and isothermal elasticities is equal to the ratio of the specific heats at constant pressure and constant volume in the case of a perfect gas. Later the result will be extended and shown to be valid for all substances. It will be seen that the isothermal elasticity of a perfect gas is equal to the pressure. In textbooks on sound it is proved that the velocity U with which sound waves travel in any medium is:

$$U = \sqrt{\frac{\text{Elasticity}}{\text{Density}}},$$

a result first obtained by Newton. This was used by him to calculate the velocity of sound in air, assuming the elasticity equal to the pressure. The result so found was much lower than the experimental value. The discrepancy was not properly accounted for until Laplace in 1816 pointed out that when sound travels through air the compressions and rarefactions take place in such rapid succession that the process is essentially adiabatic. Therefore in calculating the velocity with which the sound waves travel in a gas the adiabatic elasticity should be used. The equation for the velocity then becomes:

$$U = \sqrt{\frac{\gamma p}{\rho}},$$

where ρ is the density of the gas. By measuring the velocity of sound in a gas the ratio of the specific heats can be accurately determined. The method has been extensively developed by Partington and Shilling, to whose book the reader is referred for full details.

CHAPTER III

THE SECOND LAW OF THERMODYNAMICS

18. The Efficiency of Heat Engines.—Any mechanism for the conversion of heat into mechanical power is termed a heat engine. It was demonstrated in the previous chapter that the work obtainable in a reversible cyclic process is equal to the enclosed area on a p—v diagram. So far, however, we have not considered what proportion of the heat taken in by the working substance is converted into work. Of two engines which take in heat during the performance of a cycle of operations, the more efficient is obviously the one which converts the greater fraction of the heat absorbed into work. We are able then to define the efficiency of a heat engine as the ratio of the mechanical work done during one cycle to the heat absorbed in the cycle. That is:

$$\text{Efficiency} = \eta = \frac{W}{q_1}. \qquad . \quad . \quad . \quad . \quad . \qquad (26)$$

The problem now is to discover the method by which the greatest efficiency may be obtained, and to find an expression for the maximum efficiency theoretically possible.

Until Sadi Carnot in 1824 published his remarkable essay, *Réflexions sur la puissance motrice du feu, et sur les machines propre a développer cette puissance*, there had been no exhaustive theoretical investigation of heat engine efficiency, although the practical problem of the conversion of heat into work had been solved satisfactorily. This essay, which received but little attention when first published, may be said to have laid the foundations of thermodynamics.

Carnot showed that the most efficient engine is one in which all the operations are made in a reversible manner. He conceived the idea of a perfect engine in which these conditions held, and the cycle which this engine performs is now known as "Carnot's cycle."

19. Carnot's Cycle.—To realise Carnot's cycle it is necessary to imagine ideal conditions which can only be approximated to in practice. We shall suppose that the cycle is performed by an ideal engine consisting of a cylinder and piston which moves without any frictional forces coming into play. The engine is supposed to be made of perfectly non-conducting material except the base of the cylinder, which is a conductor. Imagine also that there are three stands, A, B, and C, the first of which, A, is constantly maintained at the temperature t_1 (the scale of temperature is immaterial), the second, B, is a non-conductor and the third, C, is constantly maintained at t_2, which is less than t_1. Attached to the piston is a rod which connects to the external system on which work is to be performed. The working substance, about which no assumptions are made, is contained in the cylinder between the piston and the conducting base. Let us start with the cylinder on the stand B, and suppose that the condition of the working substance is represented by the point *a* on the p—v diagram, Fig. 11, its temperature being t_2. The working substance is now

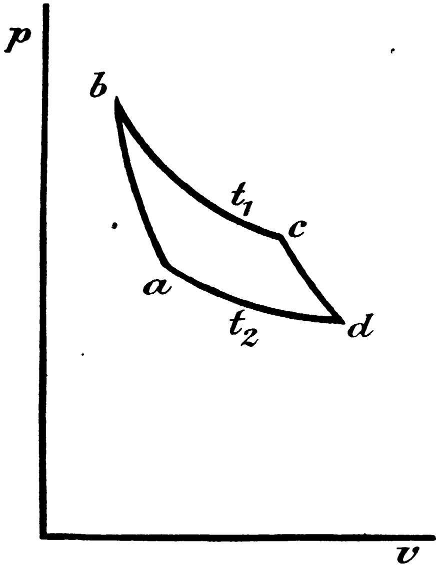

FIG. 11.

Carnot's Cycle.

made to go through four operations, two adiabatic and two isothermal.

(1) With the cylinder on the stand B compress the working substance adiabatically until its temperature rises to t_1, work being done on the substance. Let its condition at the end of this process be represented by the point *b*.

(2) Put the cylinder on the stand A and allow the working substance to expand isothermally at the temperature t_1, doing external work and taking in heat from A. Stop the expansion at any convenient point, and let the condition of the working substance now be represented by the point *c*.

(3) Again place the cylinder on B and allow the working substance to expand adiabatically until its temperature falls to t_2, its condition now being represented by the point *d*.

(4) Put the cylinder on the stand C and compress the working substance at the temperature t_2 until the conditions represented by the point *a* are again reached. Heat will be rejected to C in this process, and the cycle is completed, the working substance having been brought back to its initial condition.

If q_1 is the heat absorbed during the isothermal expansion at temperature t_1, and q_2 that rejected at temperature t_2, the work done in the cycle is equivalent to the heat which has disappeared, i.e. to $q_1 - q_2$. Hence the efficiency is given by:

$$\eta = \frac{W}{q_1} = \frac{q_1 - q_2}{q_1} = 1 - \frac{q_2}{q_1}.$$

The cycle just described is completely reversible; that is, it can be performed in the reverse direction, taking in heat at the lower temperature and rejecting heat at the higher, work in this case being done on the working substance. The amounts of heat absorbed and rejected would be exactly the same as those rejected and absorbed respectively in the previous case.

The reversibility of the operations depends upon their being carried out sufficiently slowly for the substance to be at all times in thermal and mechanical equilibrium with its surroundings. Suppose, for instance, that in one of the isothermal processes the pressure on the working substance is p. If expansion is occurring the pressure is falling, and the load on the piston must be such that if the pressure increased infinitesimally above p then compression would commence, the cycle then going in the reverse direction.

Similarly, in order for conduction of heat from the stands A and C to the cylinder to take place there must be a difference in temperature, but this must be so small that conduction just takes place and that is all. The processes may be considered as being performed by conducting the working substance through a series of equilibrium positions, any slight alteration from such a position being in the direction to guide the working substance to the next position of equilibrium.

20. The Efficiency of a Reversible Heat Engine.—From a consideration of reversible heat engines of the type already described, Carnot was led to the conclusion that no heat engine can be more efficient than a reversible one working between the same temperature limits. This is known as Carnot's Principle. The proof given below is, in essentials, the same as that given by Carnot.

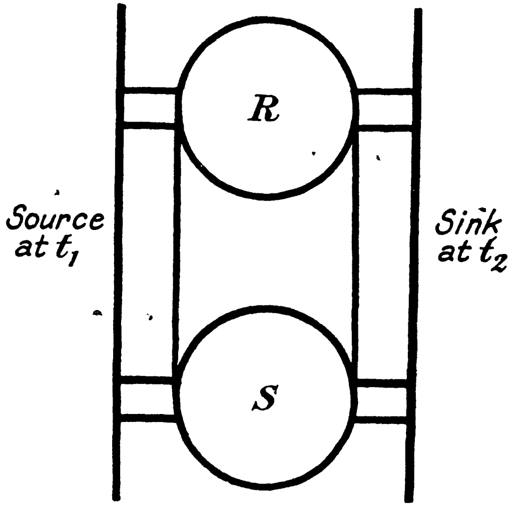

FIG. 12.

Consider two engines coupled together and working between the same temperature limits, say t_1 and t_2. Suppose that one of them, R, Fig. 12, is reversible, and the other, S, irreversible, and that S is more efficient than R. Let the engines be so arranged that the irreversible engine drives the reversible engine backwards. That is R, by working in the reverse direction, conveys heat from the sink at t_2 to the source at t_1. If now the engines are so adjusted that in a complete cycle of the coupled engines S takes an amount of heat q from the source at t_1 and R returns the same amount, S will be enabled to drive R in the reverse direction and still possess a balance of mechanical power capable of utilisation for the performance of useful work in consequence of its greater efficiency. But in the performance of this useful work there will be no net abstraction of heat from the hot source for that taken by S will be returned by R and therefore the hot source is unnecessary. That is, the two machines working together as a self-acting machine unaided by any external agency are able to perform external work without the use of a separately maintained source of heat. This Carnot concluded was contrary to experience and impossible. That is, S cannot be more efficient than R. Therefore no engine can be more efficient than a reversible engine working between the same limits of temperature, which is Carnot's Principle.

By the consideration of two reversible heat engines, say R and R′, of which one, R′, is supposed more efficient than the other, coupled in such a manner that R′ drives R reversed, the same argument shows that one cannot be more efficient than the other. That is, all reversible heat engines working between the same temperature limits have the same efficiency.

These results show that reversibility is the criterion of perfection in a heat engine in the sense that no engine can convert a greater proportion of the heat supplied into work than one working in a reversible manner. It will be noticed that no assumptions as to the nature of the working substance have been made; this is immaterial if the criterion of reversibility is satisfied. Hence we see that the greatest efficiency in the conversion of heat into work is obtained by supplying the heat to an engine working in such a manner that all its operations are reversible.

21. The Second Law of Thermodynamics.—Various alternative modes of expressing the second law of thermodynamics have been proposed from time to time. Nevertheless, it must be remembered that, however stated, the second law is a direct deduction from Carnot's Principle. The statement due to Clausius is given below as being the most convenient for general use.

"It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature."

To prove this law we can assume two engines R and S coupled together such that S drives the reversible engine R backwards as before. Let the mechanical work produced by S be just sufficient to drive R in the reverse direction, and suppose that in a complete cycle of the coupled engines S takes an amount of heat q_1 from the source whilst q_2 is returned by R. If q_2 is greater than q_1, the hot body would on the whole gain heat by the working of a self-acting machine. The supposition that q_2 is greater than q_1 is the same as the supposition that the engine S is more efficient than the reversible engine R. This, by Carnot's Principle, is impossible, and therefore q_2 cannot be greater than q_1. Thus the self-acting machine formed by coupling S and R is unable to convey heat from the low temperature sink to the high temperature source. This is equivalent to Clausius' statement of the second law.

22. Expression for the Efficiency of a Reversible Heat Engine.—We have seen that all reversible heat engines working between the same temperature limits have the same efficiency, and this is independent of the nature of the working substance. Consequently the only factors which can determine the efficiency are the temperature limits between which the engine works. If these are t_1 and t_2 the efficiency can be expressed as:

$$\eta = 1 - \frac{q_2}{q_1} = f(t_1, t_2), \quad . \quad . \quad . \quad . \quad . \quad (27)$$

where q_1 and q_2 are the quantities of heat absorbed and rejected in one cycle respectively, and $f(t_1, t_2)$ is some as yet undetermined function. By taking unity from each side of equation (27) and inverting, we can write:

$$\frac{q_1}{q_2} = F(t_1, t_2),$$

where $F(t_1, t_2)$ is a different function from $f(t_1, t_2)$.

Now suppose we have two engines, the first taking in heat q_1 at t_1 and rejecting heat q_2 at t_2, and the second taking in heat q_2 at t_2 and rejecting heat q_3 at t_3. Then:

$$\frac{q_1}{q_2} = F(t_1, t_2), \quad \frac{q_2}{q_3} = F(t_2, t_3). \quad . \quad . \quad . \quad (28)$$

If the two engines are now coupled together in such a manner that the compound engine acts as a simple engine working between the temperatures t_1 and t_3, we have:

$$\frac{q_1}{q_3} = F(t_1, t_3).$$

But by multiplication of the two equations (28):

$$\frac{q_1}{q_3} = F(t_1, t_2) \,.\, F(t_2, t_3).$$

Hence

$$F(t_1, t_3) = F(t_1, t_2) \,.\, F(t_2, t_3).$$

That is, t_2 must disappear from the right-hand side of this equation. In order that this may happen $F(t_1, t_2)$ must be of the form:

$$F(t_1, t_2) = \frac{\psi(t_1)}{\psi(t_2)},$$

and consequently:

$$\frac{q_1}{q_2} = \frac{\psi(t_1)}{\psi(t_2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

As q_1 is always greater than q_2, $\psi(t_1)$ must be greater than $\psi(t_2)$, or the function $\psi(t)$ is such that its magnitude increases with increase in temperature.

23. Kelvin's Absolute Thermodynamic Scale of Temperature.—It was realised by Lord Kelvin, then Professor Thomson, that the important relation (29) for a reversible heat engine could be used to compare the two temperatures t_1 and t_2. We have seen in Chapter I that any property which depends only upon temperature can be used to define a temperature scale. Now $\psi(t)$ is a function of the temperature only, and therefore the values of this function, if once determined for all values of t, would be sufficient to define a new scale of temperature.

Writing

$$\psi(t) = T,$$

where T is the temperature on the new scale,* we see that the ratio of any two temperatures on this scale is the same as the ratio of the heat taken in to the heat rejected in a perfect thermodynamic engine working between these temperatures as source and sink respectively.

---

* Temperatures on this scale are signified as °K.

This new scale is dependent only upon the characteristics of a reversible heat engine, and these are independent of the nature of the working substance. Hence the scale so defined is absolute in the sense that it is independent of the properties of any particular substance.

If we have a series of engines all doing the same amount of work W in a cycle, the first taking in heat q_1 at T_1 and rejecting heat q_2 at T_2, the second taking in heat q_2 at T_2 and rejecting heat q_3 at T_3, and so on, we have:

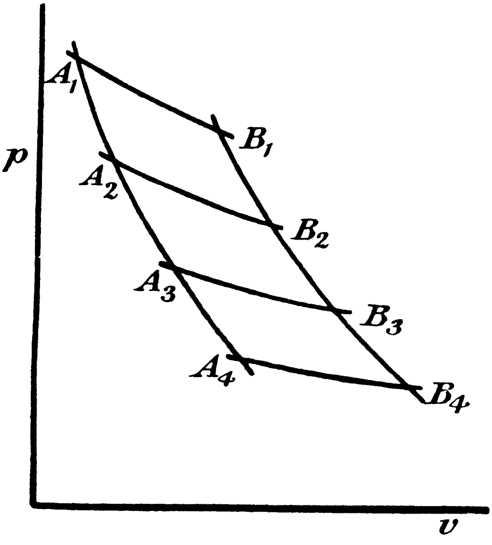

FIG. 13.

$$W = q_1 - q_2 = q_2 - q_3 = \ldots$$

and

$$\frac{q_1}{T_1} = \frac{q_2}{T_2} = \frac{q_3}{T_3} = \ldots \qquad (30)$$

and hence

$$T_1 - T_2 = T_2 - T_3 = \ldots$$

This can be illustrated graphically as in Fig. 13. A_1 A_2 A_3 and B_1 B_2 B_3 are two adiabatics for some substance, and $A_1 B_1$, $A_2 B_2$,

A_3 B_3, etc., are isothermals drawn so that the areas of the cycles so formed are equal. Then the isothermals correspond to equal differences in temperature.

The scale defined in the above manner is the absolute thermodynamic scale, or, as it is sometimes known, Kelvin's absolute scale. This manner of reckoning temperature leads to the idea of an absolute zero, for if the heat rejected by an engine, q_n say, is zero, T_n is also zero. But for q_n to be zero means that all the heat supplied to the engine has been converted into work, and by the first law of thermodynamics the heat which disappears and the work produced must be equivalent. Hence negative temperatures are impossible, and the zero on this scale is the lowest possible limit of temperature.

Having found the zero from which temperatures are now to be measured, the only thing which remains arbitrary is the size of the degree, and this may be fixed in the same way as for an ordinary temperature scale by choosing a certain number of degrees between two fixed temperatures. The method adopted for all scientific work is to divide the temperature interval between the ice and steam points into one hundred degrees. As soon as the number corresponding to one of these points has been determined, the numerical value of every other temperature is fixed independently of the characteristics of any particular substance.

24. Efficiency and Available Energy.—Using the thermodynamic scale of temperature the expression for the efficiency of a Carnot cycle takes a very simple form. From equation (26) we have:

$$\eta = \frac{W}{q_1} = \frac{q_1 - q_2}{q_1},$$

which by substitution from (30) becomes:

$$\eta = \frac{T_1 - T_2}{T_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

This is the maximum efficiency theoretically attainable by an engine taking in heat at temperature T_1 and rejecting heat at T_2. No real engine ever has such a high efficiency, but this theoretical limit is of great importance in showing what the efficiency would be if the criterion of reversibility were satisfied.

For an engine taking in heat q_1 at T_1 and working between the temperature limits T_1 and T_2, the maximum amount of work obtainable from the heat taken in is $q_1\left(1 - \frac{T_2}{T_1}\right)$. If T_2 is zero all the heat taken in is converted into work, i.e. the efficiency is unity, but for any other temperature than zero the quantity $\left(1 - \frac{T_2}{T_1}\right)$ is a fraction, and this fraction of the heat taken in at the higher temperature represents all the heat that can be used in the performance of useful work. The quantity $q_1\left(1 - \frac{T_2}{T_1}\right)$, where q_1 is the heat available at the temperature T_1 and T_2 is the lowest available temperature, is known as the available energy.

25. Carnot's Cycle for a Perfect Gas.—Consider a Carnot cycle being performed with a perfect gas as the working substance. Suppose that the temperatures of the two isothermals, Fig. 11, are θ_1 and θ_2 on the gas scale, and T_1 and T_2 on the absolute thermodynamic scale. The equations to the curves *bc* and *ad* can then be written:

$$pv = R\theta_1 \quad \text{and} \quad pv = R\theta_2.$$

Also the adiabatics *ba* and *cd* are given by the equations:

$$pv^\gamma = k_1 \quad \text{and} \quad pv^\gamma = k_2.$$

Suppose the cycle is started from the point *b*. Then the heat taken in by the perfect gas in expanding from v_b at *b* to v_c at *c* is the same as the external work done, as the internal energy is independent of the volume. Thus by equation (25) the heat absorbed is:

$$q_1 = R\theta_1 \log \frac{v_c}{v_b}. \qquad \ldots \ldots \quad (32)$$

Similarly the heat given out when traversing the lower isothermal from *d* to *a* is:

$$q_2 = R\theta_2 \log \frac{v_d}{v_a}. \qquad \ldots \ldots \quad (33)$$

Now at the point *b*:

$$pv = R\theta_1 \quad \text{and} \quad pv^\gamma = k_1,$$

and at c:

$$pv = R\theta_1 \quad \text{and} \quad pv^\gamma = k_2.$$

Hence

$$v_b^{\gamma-1} = \frac{k_1}{R\theta_1},$$

and

$$v_c^{\gamma-1} = \frac{k_2}{R\theta_1}.$$

Therefore

$$\frac{v_c}{v_b} = \left(\frac{k_2}{k_1}\right)^{\frac{1}{\gamma-1}}.$$

Similarly

$$\frac{v_d}{v_a} = \left(\frac{k_2}{k_1}\right)^{\frac{1}{\gamma-1}}$$

or

$$\frac{v_c}{v_b} = \frac{v_d}{v_a}.$$

Consequently, dividing equation (33) into (32) we have:

$$\frac{q_1}{q_2} = \frac{\theta_1}{\theta_2}.$$

We have already shown that if temperatures are measured on the absolute thermodynamic scale:

$$\frac{q_1}{q_2} = \frac{T_1}{T_2}.$$

Therefore the ratio of the temperatures on the perfect gas scale is the same as the ratio of the temperatures on the absolute thermodynamic scale. If the size of the degree is made the same on each scale, the number expressing the temperature will be the same on either scale. The so-called permanent gases such as hydrogen and nitrogen behave approximately as perfect gases, so that the readings of thermometers using these gases as the thermometric substance differ but little from the absolute thermodynamic temperature. In Chapter V it is shown how the temperatures as measured by a gas thermometer can be corrected to give the absolute thermodynamic temperature. In the following work absolute temperature on either scale will be denoted by T unless the contrary is specifically expressed.

26. The Theorem of Clausius.—For a simple substance performing a Carnot cycle it has been shown that

$$\frac{q_1}{T_1} = \frac{q_2}{T_2},$$

which can be written:

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0,$$

if heat absorbed is considered positive and heat rejected negative.

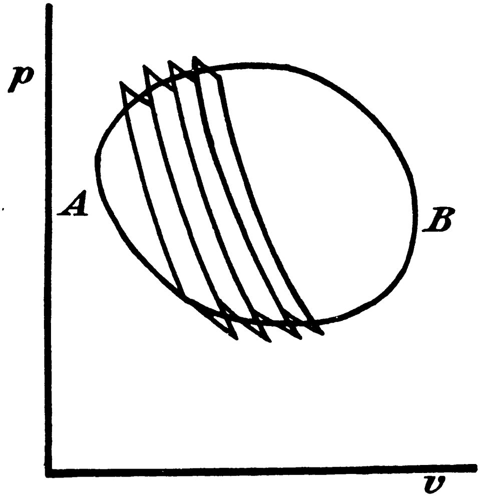

FIG. 14.

For a general reversible cyclic process the heat is not all absorbed and rejected at two definite temperatures, but is taken in and given out at temperatures which vary continuously. The above result for a Carnot cycle can easily be extended for all reversible cycles by a method due to Clausius.

Consider the cycle shown in Fig. 14. Instead of following the smooth curve A B, replace it by a series of infinitesimal isothermal changes as shown by the zigzag curve. By drawing adiabatic lines across the closed curve it can be divided up into an infinite number of extremely small Carnot cycles, and making the portions of isothermals sufficiently small the broken curve will approximate as closely as we please to the continuous curve. For any one of the small Carnot cycles, if δq_1 is the heat absorbed at T_1 and $-\ \delta q_2$ that rejected at T_2, we have:

$$\frac{\delta q_1}{T_1} + \frac{\delta q_2}{T_2} = 0.$$

Or taking the sum for all the cycles:

$$\Sigma \frac{\delta q}{T} = 0.$$

This relation is true for any reversible cyclic transformation.

27. **Entropy.**—Imagine a substance being transformed from a state A to a state B by a reversible path. Let us first suppose that in the change only an infinitesimal amount of heat is absorbed at a constant temperature T. If the heat absorbed is δq, the entropy of the substance is said to have changed by the amount $\frac{\delta q}{T}$. This must be regarded as the definition of entropy. If the substance absorbs a finite amount of heat the change in entropy is obtained by evaluating the sum $\Sigma \frac{\delta q}{T}$ between the initial and final states along a reversible path.

Consider two reversible paths, 1 and 2, Fig. 8, by which the substance may be transformed from the state A to the state B. Let the change of entropy by the path 1 be S and by the path 2, S'. The two paths form a closed reversible cycle, and for the whole cycle the change of entropy must be zero by our previous result. Hence

$$S - S' = 0,$$

or

$$S = S'.$$

That is, the change of entropy between any two states is independent of the reversible path chosen for the transformation. The entropy, then, must be a function of the state of the substance in the same way as the internal energy. This is expressed mathematically by saying that $\frac{\delta q}{T}$ is a perfect differential of some function S, such that

$$\frac{\delta q}{T} = dS, \quad \dots\dots\dots \quad (34)$$

and the value of the sum taken along any reversible path joining A and B is:

$$\sum_{A}^{B} \frac{\delta q}{T} = S_B - S_A.$$

In an isothermal change the increase in entropy is $\frac{q}{T}$, where q is the heat absorbed at temperature T.

For a reversible adiabatic change there is no gain or loss of heat and therefore no change in entropy. For this reason reversible adiabatic processes are sometimes called *isentropic* processes.

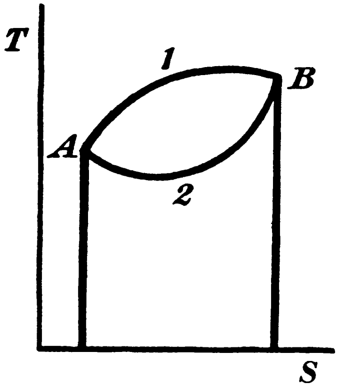

FIG. 15.

28. Temperature - Entropy Diagrams.—Up to the present we have represented all cyclic processes on p—v diagrams. For many practical purposes temperature-entropy diagrams are more convenient.

The state of a substance is represented by a point whose coordinates are S, T, Fig. 15.

Let the substance pass from the state A to the state B by the reversible path 1. The heat taken in is:

$$\Sigma\delta q = \Sigma T dS = \int_A^B T dS.$$

That is, the heat taken in is equal to the area under the curve 1.

Similarly the heat given out in passing from B to A by the reversible path 2 is equal to the area under the curve 2.

In the cycle the net amount of heat which disappears is the difference between these two areas. As the internal energy of the substance is unchanged at the end of the cycle the heat which disappears must all be used in doing external work, or the enclosed area on a temperature-entropy diagram represents the work done in the cycle.

For a Carnot cycle the temperature-entropy diagram is of a particularly simple form. The isothermals are lines parallel to the entropy axis and the adiabatic lines parallel to the temperature axis. The cycle is a rectangle, Fig. 16, where the letters correspond to those used in Fig. 11. The form of a Carnot cycle on a temperature-entropy diagram is independent of the nature of the working substance.

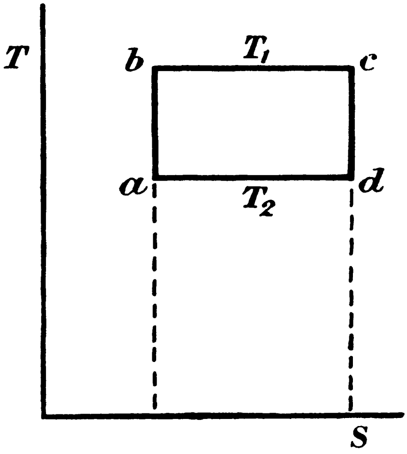

FIG. 16.
Carnot's Cycle.

29. Entropy of a Perfect Gas.—For a perfect gas, the internal energy of which depends only upon the temperature, the heat required to produce an infinitesimal change is given by equation (22), as:

$$\delta q = c_p dT - v dp,$$

and substituting for δq from equation (34) we have:

$$TdS = c_p dT - v dp,$$

or

$$dS = \frac{c_p}{T} dT - \frac{v}{T} dp.$$

Substituting in the second term on the right-hand side from the perfect gas equation:

$$pv = RT,$$ ✓

we see that

$$dS = \frac{c_p}{T} dT - R \,.\, \frac{dp}{p},$$

which on integration becomes

$$S = \int^T \frac{c_p}{T} dT - R \log p + C, \quad . \quad . \quad . \quad . \qquad (35)$$

where C is a constant of integration.

If it is assumed that the specific heat at constant pressure is independent of the temperature, the integration can be completed and the expression for the entropy written:

$$S = c_p \log T - R \log p + C.$$

Similarly, starting from the equation

$$\delta q = c_v dT + p dv,$$

the entropy is found to be

$$S = \int^T c_v \frac{dT}{T} + R \log v + C',$$

or assuming as before that the specific heat at constant volume is independent of the temperature:

$$S = c_v \log T + R \log v + C'.$$

30. Adiabatic and Isothermal Elasticities.—As an illustration of the use of the entropy the ratio of the adiabatic and isothermal elasticities of any substance will now be found.

Since the change in entropy is independent of the path adopted for the transformation we may write the small increment in entropy which occurs when the pressure and volume of the body increase by the amounts dp and dv in the form

$$dS = \left(\frac{dS}{dp}\right)_v dp + \left(\frac{dS}{dv}\right)_p dv.$$

For an adiabatic change the entropy is constant and we then have

$$\left(\frac{dS}{dp}\right)_v \cdot \left(\frac{dp}{dv}\right)_S = - \left(\frac{dS}{dv}\right)_p.$$

By the definition of elasticity of Section 17 we have therefore:

$$K_S = - v \cdot \left(\frac{dp}{dv}\right)_S = v \cdot \left(\frac{dS}{dv}\right)_p \Big/ \left(\frac{dS}{dp}\right)_v$$

$$= v \cdot \left(\frac{dS}{dT}\right)_p \cdot \left(\frac{dT}{dv}\right)_p \Big/ \left(\frac{dS}{dT}\right)_v \cdot \left(\frac{dT}{dp}\right)_v,$$

where K_S is the adiabatic elasticity. This last equation may be written in the form

$$K_S = v \cdot \frac{c_p}{c_v} \cdot \left(\frac{dT}{dv}\right)_p \Big/ \left(\frac{dT}{dp}\right)_v, \quad . \quad . \quad . \quad . \quad . \quad (36)$$

since

$$c_p = T \left(\frac{dS}{dT}\right)_p \text{ and } c_v = T \left(\frac{dS}{dT}\right)_v.$$

Writing the change of temperature of a body in terms of the changes in pressure and volume we have:

$$dT = \left(\frac{dT}{dp}\right)_v dp + \left(\frac{dT}{dv}\right)_p dv.$$

Hence for an isothermal change, i.e. $dT = 0$,

$$\left(\frac{dT}{dp}\right)_v \cdot \left(\frac{dp}{dv}\right)_T = -\left(\frac{dT}{dv}\right)_p$$

or

$$K_T = v \cdot \left(\frac{dT}{dv}\right)_p \Big/ \left(\frac{dT}{dp}\right)_v \quad . \quad . \quad . \quad . \quad . \quad (37)$$

Dividing equation (36) by equation (37) we obtain the ratio of the adiabatic and isothermal elasticities, as:

$$\frac{K_S}{K_T} = \frac{c_p}{c_v} = \gamma.$$

This is a perfectly general result, true for all substances.

31. Loss of Available Energy and Increase of Entropy. —It has been shown that the heat which disappears in the performance of a reversible cycle is all used in the development of mechanical power which can be utilised in the performance of external work. If frictional forces come into action part of the mechanical energy developed is used in overcoming these forces; their result is that the mechanical energy so used is converted into heat and wasted, and not only is it irrecoverable from the system by a reversal of the processes, but still more mechanical energy is used in overcoming the frictional forces, which always act so as to oppose any change. Thus we see that any process in which these forces act is irreversible, and if the process is cyclic the efficiency is less than for a reversible cycle working between the same temperature limits.

Suppose we have a cycle taking in heat δq_1 at a temperature T_1, and rejecting heat δq_2 at T_2. If T_0 is the lowest available temperature the available energy, or motivity, of the heat δq_1 at T_1, as was shown in Section 24, is:

$$\delta q_1\left(1 - \frac{T_0}{T_1}\right)$$

and the motivity of the heat δq_2 at T_2 is:

$$\delta q_2\left(1 - \frac{T_0}{T_2}\right).$$

Hence the total change in motivity, or energy available for the performance of external work, is:

$$\delta q_1 - \delta q_2 - T_0\left(\frac{\delta q_1}{T_1} - \frac{\delta q_2}{T_2}\right).$$

If the working substance performs any closed finite cycle this expression becomes:

$$q_1 - q_2 - T_0\sum\frac{\delta q}{T},$$

where q_1 is the whole quantity of heat taken in and q_2 the whole quantity of heat given out. For a reversible cycle the sum vanishes and the total loss in motivity is $q_1 - q_2$. For an irreversible cycle the loss in motivity must be greater than for a reversible cycle, and therefore the summation taken round an irreversible cycle must be negative. In such a cycle there is a waste or dissipation of mechanical energy of the positive value:

$$D = - T_0\sum\frac{\delta q}{T}.$$

We can consider the same problem by calculating the entropy changes. As the efficiency of an irreversible cycle is less than that of a reversible cycle working between the same temperature limits, we have:

$$\frac{q_1 - q_2}{q_1} < \frac{T_1 - T_2}{T_1},$$

or

$$\frac{q_1}{T_1} - \frac{q_2}{T_2} < 0.$$

If heat absorbed is regarded as being positive and heat rejected negative, this becomes:

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} < 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

So far the transference of heat from and to the external bodies acting as source and sink respectively has not been considered. In order to simplify the problem it may be supposed that these heat transfers take place in a reversible manner, the irreversibility of the cycle as a whole arising from some other cause. In this case the hot body would lose entropy of amount $\frac{q_1}{T_1}$ in one cycle and the cold body gain entropy of amount $\frac{q_2}{T_2}$. The total gain of entropy throughout the whole system, including the source and sink, in the performance of one cycle of operations would therefore be

$$\frac{q_2}{T_2} - \frac{q_1}{T_1},$$

since the working substance having returned to its initial state will have suffered no entropy change. Adopting the same sign convention as before we have

$$\text{Total entropy change} = -\left(\frac{q_1}{T_1} + \frac{q_2}{T_2}\right) > 0$$

by the use of equation (38).

The result of equation (38) can be extended to the case of a general irreversible cyclic process by the same method as was employed in proving the theorem of Clausius. The general equation for any reversible cycle is:

$$\sum \frac{\delta q}{T} < 0.$$

As before, the increase in entropy of the system as a whole is $-\sum \frac{\delta q}{T}$, and this will obviously be a positive quantity. That is, in all irreversible cyclic processes there is an increase in entropy. It will be noticed that the amount of energy dissipated is the lowest available temperature times the increase in entropy.

In the above we have considered only cyclic processes. It may easily be shown, however, that any irreversible process is accompanied by an increase in entropy. Consider two conditions of a substance represented by the points A and B on a *p-v* diagram such as Fig. 8. It will be supposed that the substance can be transformed from the state A to the state B by the irreversible path 1 and returned to its initial state by the reversible path 2. The two paths together form a closed irreversible cycle. For this cycle we have

$$\sum \frac{\delta q}{T} < 0,$$

and the summation may be divided into two parts; one corresponding to the transformation from A to B by the irreversible path and the other to that for the reversible path from B to A. Hence the inequality may be written

$$\sum_{A}^{B} \frac{\delta q}{T} + S_A - S_B < 0.$$

If as before it is supposed that the transfer of heat from or to the other bodies in the whole system takes place in a reversible manner, the change of entropy in these other bodies whilst the substance is being transformed from A to B by the irreversible path is $-\sum_{A}^{B} \frac{\delta q}{T}$, and the substance itself undergoes an entropy change of amount $S_B - S_A$. Hence the total change of entropy is

$$-\sum_{A}^{B} \frac{\delta q}{T} + S_B - S_A,$$

which by the above inequality is greater than zero, *i.e.* a positive quantity corresponding to an increase in entropy as the transformation from A to B takes place.

In the same way we may calculate the dissipation in mechanical energy in going from A to B by the irreversible path. For the cycle formed by the irreversible path 1 and the reversible path 2 the dissipation of mechanical energy has already been proved to be

$$-T_0 \sum \frac{\delta q}{T}$$

where the summation has to be taken around the whole cycle.

Any loss of available energy will occur during the performance of the irreversible part of this cycle only, for when the substance is describing the reversible path a slight alteration of the conditions will reverse the process and the energy will be recoverable from the system. Hence the above expression represents the loss of available energy in going from A to B by the irreversible path. It may be written

$$-T_0\left\{\sum_{A}^{B}\frac{\delta q}{T}+S_A-S_B\right\},$$

since $\sum_{B}^{A}\frac{\delta q}{T}$ along the reversible path is the change of entropy between B and A. If the transfers of heat in the irreversible process are themselves reversible $-\sum_{A}^{B}\frac{\delta q}{T}$ is the increase in entropy of the other parts of the system, and once again the loss of available energy is the lowest available temperature times the total increase in entropy.

32. Examples of Irreversible Processes.—It is interesting to consider various special cases of irreversible processes and calculate the dissipation of mechanical energy and increase of entropy.

(i) *Joule's Experiment.*—In Joule's experiment on the internal energy of gases, a gas under compression was allowed to rush into a vacuum as described in Chapter II. If the gas is supposed perfect the temperature and internal energy are unchanged.

To restore to initial conditions work would have to be done on the gas to compress it from its final volume $(v + v')$ to its initial volume v, where v and v' are the specific volumes of the gas in containers A and B, Fig. 10, respectively. This could be done by means of a piston in B, which would slowly compress the gas. As the temperature and therefore the internal energy of the perfect gas are unchanged we have the relation:

$$\delta q = pdv,$$

which can be integrated by substitution from the perfect gas equation. Doing this we see that the heat which would have been taken in by the gas in expanding from a volume v to $(v + v')$ along a reversible path is:

$$q = \int_{v}^{v + v'} p\,dv = RT\int_{v}^{v + v'} \frac{dv}{v} = RT \log \frac{v + v'}{v}. \quad . \quad . \quad . \quad (39)$$

In restoring the initial conditions this amount of heat would have to be withdrawn from the gas whilst an equivalent amount of work was done on the gas. The net result would be to have the gas in its initial condition and an amount of heat q at the temperature T. If T_0 is the lowest available temperature the available energy of this heat is $q\left(1 - \frac{T_0}{T}\right)$; as work equivalent to q has been done on the gas, the amount of heat wasted in the original process is obviously $q - q\left(1 - \frac{T_0}{T}\right)$, or $q\frac{T_0}{T}$. That is, the dissipation of mechanical energy is:

$$q\frac{T_0}{T} = RT_0 \log \frac{v + v'}{v},$$

by substitution from (39).

Considering the changes in entropy we have, since E is a function of the temperature only:

$$T dS = p dv,$$

or

$$dS = \frac{p}{T} dv.$$

Hence

$$\text{Change in entropy} = S_2 - S_1 = R\int_{v}^{v + v} \frac{dv}{v} = R \log \frac{v + v'}{v}.$$

As before the dissipation of mechanical energy is the lowest available temperature times the increase in entropy.

This experiment illustrates an interesting principle. Although in the expansion there is no heat exchange between the gas and its surroundings there is an increase in the entropy. The reason for this is that the gas is not allowed to expand in a reversible manner, and to find the change in entropy the path over which the summation $\sum \frac{\delta q}{T}$ has to be evaluated must be reversible.

(ii) *Conduction of Heat.*—Let a quantity of heat q be transferred from one face of a slab of material at temperature T_1 to an opposite face at temperature T_2 by conduction. The available energy before the transfer is:

$$q\left(1 - \frac{T_0}{T_1}\right),$$

and after

$$q\left(1 - \frac{T_0}{T_2}\right),$$

if T_0 is the lowest available temperature.

Hence the loss in available energy is:

$$q\,T_0\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

which is positive as T_1 must be greater than T_2 for conduction to occur.

If the changes of entropy of the hot and cold faces are considered, the hot face loses entropy of amount $\frac{q}{T_1}$ whilst the cold face gains $\frac{q}{T_2}$, the increase in entropy being:

$$q\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

which is the loss of available energy divided by T_0.

33. Increase of Entropy in Natural Processes.—It has been shown that in all processes, other than those which are perfectly reversible, there is an increase in entropy or loss of available energy. In practice no heat engine is perfectly reversible, the efficiency always being less than the theoretical limit. Necessarily, therefore, when it is attempted to transform heat into mechanical energy some of it is wasted and is irrecoverable in the form of mechanical effort. The energy in the universe is constantly undergoing transformations, and these for the most part are irreversible, entailing a loss of available energy. The view of Clausius, "the entropy of the universe tends towards a maximum," and that of Thomson, "available energy is always lost, never gained," express the same natural principle.

CHAPTER IV

THERMODYNAMIC FUNCTIONS

34. Calculation of Internal Energy.—It was pointed out in Chapter II that the internal energy of a substance cannot be directly measured by a calorimetric method. Using the first law of thermodynamics in the form

$$\delta q = dE + \delta W,$$

changes in internal energy can be found if the quantities δq and δW are measured. As an example let us calculate the change in internal energy when unit mass of water is converted into steam at 0° C. The heat given to the water is the latent heat of steam at 0° C., and from tables* this is 594·27 calories per gram.

The external work done is an expansion against the saturation pressure of the liquid. The saturation pressure of water at 0° C. is 615·1 dynes per sq. cm., and the volume of one gram of steam at the same temperature, 204,510 c.c.s., in comparison with which the volume of one gram of water, 1 c.c., is negligible. Hence the external work done in the expansion is given by:

$$pdv = \frac{615\cdot 1 \times 204{,}510}{4\cdot 185 \times 10^7} = 30\cdot 06 \text{ calories},$$

the factor in the denominator being the mechanical equivalent of heat to convert ergs to calories. Hence as

$$dE = \delta q - \delta W,$$

$$\begin{aligned} \text{Change in internal energy} &= 594\cdot 27 - 30\cdot 06, \\ &= 564\cdot 21 \text{ calories.} \end{aligned}$$

As the internal energy of water is usually reckoned as zero at 0° C. and under its own saturation pressure, 564·21 calories per gram is the internal energy of saturated steam at 0° C. The internal energy E per unit mass is commonly expressed in gram calories per gram or pound calories per pound, but the Centigrade unit of internal energy may be more conveniently referred to as the calorie-Centigrade, as it is obviously independent of the unit of mass.

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* H. L. Callendar, *The Properties of Steam.*

35. Total Heat.*—The total heat of a substance is defined as the sum $E + pv$, and will be denoted by the letter H. The unit is the same as for internal energy. For the purposes of engineers the total heat is a more important quantity than the internal energy, and can be measured by calorimetric methods if some state is arbitrarily chosen as that of zero total heat. The term pv is the work done in expanding the substance from zero volume to the volume v against the pressure p; it can also be regarded as the work done in pumping a fluid into an enclosure against a steady pressure.

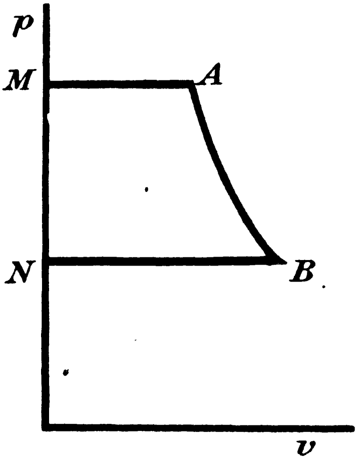

FIG. 17.

As

$$H = E + pv,$$
$$dH = dE + pdv + vdp,$$

or

$$dH = \delta q + vdp. \quad . \quad . \quad . \quad . \quad . \quad (40)$$

If the pressure is constant the second term on the right-hand side is zero, and the change of total heat at constant pressure is equal to the heat taken in.

The condition for adiabatic expansion is $\delta q = 0$. Hence for an adiabatic change

$$dH = vdp.$$

The change of total heat for a finite adiabatic expansion is obtained by integration. Thus

$$H_A - H_B = \int_B^A vdp = \text{area ABNM (Fig. 17).}$$

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* This quantity is sometimes called the "Heat Content," and also the "Enthalpy."

The quantity $H_A - H_B$ is known in engineering practice as the adiabatic heat drop.

36. The Equation of Steady Flow.—A simple illustration of the law of conservation of energy is provided by the steady flow of a liquid. Suppose a fluid is flowing through an enclosure such as that of Fig. 18, entering at A with a steady velocity U_1 at a constant pressure p_1 and specific volume v_1, and leaving at B with steady velocity U_2 at constant pressure p_2 and specific volume v_2. When the flow has become steady the masses flowing in at A and out at B in the same time must be equal if there is no leakage or other outlet.

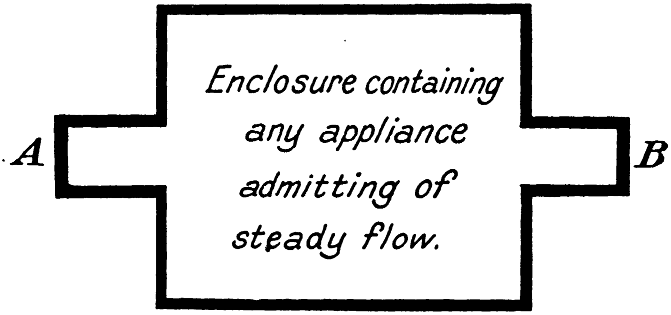
A
Enclosure containing any appliance admitting of steady flow.
B

FIG. 18.

The energy entering the enclosure at A per unit mass is $E_1 + p_1v_1 + U_1^2/2$, the sum of the internal energy E_1, the work p_1v_1, and the kinetic energy $U_1^2/2$ in the initial state. Similarly the energy per unit mass leaving the enclosure at B is the total energy $E_2 + p_2v_2 + U_2^2/2$ in the final state. Any difference between the total energy entering and the total energy leaving must, by the law of conservation of energy, be accounted for by the sum of the external loss of heat q_x measured per unit mass passing through, and the external work W done by the appliance, also measured per unit mass.

Thus

$$E_1 + p_1v_1 + \frac{U_1^2}{2} = E_2 + p_2v_2 + \frac{U_2^2}{2} + q_x + W,$$

or by the definition of total heat:

$$H_1 - H_2 = \tfrac{1}{2}(U_2^2 - U_1^2) + q_x + W. \quad . \quad . \quad (41)$$

That is, for steady flow the drop in total heat is equal to the gain of kinetic energy together with the external heat loss and external work.

A number of special applications of equation (41) are discussed below.

(i) *The Throttle.*—If the fluid is forced through a small aperture, a porous plug or simple throttle valve, the function of which is merely to reduce the pressure without loss of heat, gain of velocity, or performance of external work, the terms on the right-hand side become zero and the simple result that the total heat remains constant, or $H_1 = H_2$ is obtained. This is the condition which holds in the Joule-Thomson "porous plug" experiment (Chapter V).

(ii) *The Nozzle.*—The object of a nozzle as employed in an impulse turbine is to convert as much as possible of the energy into the kinetic form without any external work being done or heat loss. Putting q_x and W equal to zero we obtain the condition:

$$H_1 - H_2 = \tfrac{1}{2}(U_2^2 - U_1^2),$$

or the kinetic energy generated is equal to the drop in total heat.

(iii) *The Turbine.*—The object of the turbine is to obtain the maximum amount of external work without heat loss or excessive waste of kinetic energy. Putting $q_x = 0$ and $U_1 = U_2$, we have:

$$H_1 - H_2 = \mathrm{W}$$

or the external work is equal to the drop in total heat. In practice it is impossible to attain these ideal conditions, as there is always some heat loss, and usually the condition $U_1 = U_2$ is not true.

37. Calculation of Total Heat.—Once the internal energy of a substance has been found it is a matter of ease to calculate the total heat, since it only means the addition of the term pv. Reverting to the case of saturated steam at 0° C. we have already seen that the internal energy per unit mass is 564·21 calories. The term pv is 30·06 calories, the external work done when one gram of water is vaporized at 0° C., as the water volume is negligible in comparison with the volume of the steam. Hence the total heat of saturated steam at 0° C. is 594·27 calories per unit mass, if water at 0° C. and under its own saturation pressure is taken as having zero total heat.

The total heat in this case could have been obtained much more simply. By equation (40) we have:

$$dH = \delta q + vdp.$$

Now the water is supposed to be vaporized under its own saturation pressure, i.e. p constant. Hence the change in total heat is equal to the heat transferred to the water to vaporize it. That is, the latent heat of 594·27 calories per unit mass.

In any change of state, such as vaporization or fusion, the pressure is constant and therefore the change in total heat between the initial and final states is equal to the latent heat for the particular transformation.

38. The Thermodynamic Potentials.—Two functions of great utility in thermodynamics are the thermodynamic potentials* at constant volume and constant pressure.

(i) *The Thermodynamic Potential at Constant Volume.*—The thermodynamic potential at constant volume, A, is defined by the equation:

$$A = E - TS. \qquad (42)$$

Differentiating we have:

$$dA = dE - TdS - SdT,$$

and using equations (16) and (34):

$$dA = -pdv - SdT. \qquad (43)$$

In an isothermal change the second term on the right-hand side vanishes as T is constant. Denoting by W the amount of work obtainable from a system in a reversible isothermal change between the states A and B, we have:

$$\int_A^B dA = -\int_A^B pdv = -W.$$

By the definition of A it depends only upon the state of the substance and not upon the path adopted to effect a transformation; hence the previous equation can be written:

$$A_B - A_A = -W,$$

---

* The reason for the name appears in Chapter VII.

or the decrease in the function A in a reversible isothermal process is equal to the amount of work obtainable in that process. For this reason the function A has been termed the "free energy" of the system.

Since

$$dA = -pdv - SdT,$$

$$\left(\frac{dA}{dT}\right)_v = -S.$$

Substituting this value of S in (42) we have:

$$A = E + T\left(\frac{dA}{dT}\right)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

This equation was formulated in 1855 by Thomson, after whom it is named, and has since become of great importance in the application of thermodynamics to physical chemistry.

(ii) *The Thermodynamic Potential at Constant Pressure.*—The thermodynamic potential at constant pressure, G, is defined by the equation:

$$G = E - TS + pv \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

Differentiating we have:

$$dG = dE - TdS - SdT + pdv + vdp,$$

and using equations (16) and (34):

$$dG = vdp - SdT. \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

In an isothermal change at constant pressure $dG = 0$, i.e. G is constant.

39. The Thermodynamic Relations.—We have already deduced the equations:

$$dE = TdS - pdv,$$
$$dA = -pdv - SdT,$$
$$dH = TdS + vdp,$$
$$dG = vdp - SdT.$$

Each of the four quantities E, H, A, and G is a function of the independent variables which define the state of the substance only, independent of the path by which it has reached its particular condition. Consequently we are able to apply the condition for a complete differential, equation (9), to each of the above equations. Thus, using this condition, we obtain:

$$\left.\begin{aligned}\left(\frac{dT}{dv}\right)_S &= -\left(\frac{dp}{dS}\right)_v\\ \left(\frac{dS}{dv}\right)_T &= \left(\frac{dp}{dT}\right)_v\\ \left(\frac{dT}{dp}\right)_S &= \left(\frac{dv}{dS}\right)_p\\ \left(\frac{dS}{dp}\right)_T &= -\left(\frac{dv}{dT}\right)_p\end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \quad (47)$$

These are Maxwell's four thermodynamic relations.

The relations are somewhat difficult to memorize, but the student should endeavour to do so, as they are of great importance and will frequently be used in subsequent chapters.*

40. The Specific Heat Equations.—The specific heats of a substance are not, in general, constants, but depend upon the conditions to which the substance is subjected. From purely thermodynamical reasoning we are able to express the variation in terms of other properties of the substance, the equations so deduced being of importance in experimental work.

(i) *Specific Heat at Constant Volume.*—By the first law we have:

$$\delta q = dE + pdv,$$

and dE can be expressed in the form:

$$dE = \left(\frac{dE}{dT}\right)_v dT + \left(\frac{dE}{dv}\right)_T dv,$$

whence by substitution:

$$\delta q = \left(\frac{dE}{dT}\right)_v dT + \left\{\left(\frac{dE}{dv}\right)_T + p\right\} dv. \quad . \; . \quad (48)$$

---

* A useful mnemonic is the word SPorTiVe. By going round this word cyclically the four relations may be obtained. The suffixes present no difficulty, as in each case they are the opposite denominator symbol.

If the volume is constant the second term on the right-hand side vanishes and we have on division by dT:

$$c_v = \left(\frac{\delta q}{dT}\right)_v = \left(\frac{dE}{dT}\right)_v \quad . \quad . \quad . \quad . \quad . \quad (49)$$

Replacing the bracket of equation (48) by b this now becomes:

$$\delta q = c_v dT + b dv,$$

or

$$dS = \frac{c_v}{T} dT + \frac{b}{T} dv.$$

But dS can be written:

$$dS = \left(\frac{dS}{dT}\right)_v dT + \left(\frac{dS}{dv}\right)_T dv$$

Hence

$$\frac{b}{T} = \left(\frac{dS}{dv}\right)_T,$$

$$= \left(\frac{dp}{dT}\right)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

by the second thermodynamic relation.

Therefore:

$$dS = \frac{c_v}{T} dT + \left(\frac{dp}{dT}\right)_v dv,$$

and as dS is a complete differential:

$$\frac{d}{dv}\left(\frac{c_v}{T}\right)_T = \frac{d}{dT}\left(\frac{dp}{dT}\right)_v,$$

or

$$\left(\frac{dc_v}{dv}\right)_T = T\left(\frac{d^2p}{dT^2}\right)_v . \quad . \quad . \quad . \quad . \quad . \quad (51)$$

(ii) *Specific Heat at Constant Pressure.*—From equation (40) we have:

$$\delta q = dH - vdp,$$

and expressing dH in terms of the variation in temperature and pressure this becomes:

$$\delta q = \left(\frac{dH}{dT}\right)_p dT + \left\{\left(\frac{dH}{dp}\right)_T - v\right\}dp. \quad . \quad . \quad . \qquad (52)$$

If the pressure is constant we have similarly to before:

$$c_p = \left(\frac{\delta q}{dT}\right)_p = \left(\frac{dH}{dT}\right)_p. \quad . \quad . \quad . \quad . \quad . \qquad (53)$$

Equation (51) may now be written:

$$\delta q = c_p dT + b'dp,$$

or

$$dS = \frac{c_p}{T}dT + \frac{b'}{T}dp.$$

Hence

$$\frac{b'}{T} = \left(\frac{dS}{dp}\right)_T$$

$$= -\left(\frac{dv}{dT}\right)_p,$$

by the fourth thermodynamic relation.
Therefore:

$$dS = \frac{c_p}{T}dT - \left(\frac{dv}{dT}\right)_p dp.$$

Applying the condition for a complete differential as before:

$$\frac{d}{dp}\left(\frac{c_p}{T}\right)_T = -\frac{d}{dT}\left(\frac{dv}{dT}\right)_p,$$

or

$$\left(\frac{dc_p}{dp}\right)_T = -T\left(\frac{d^2v}{dT^2}\right)_p. \quad . \quad . \quad . \quad . \quad . \qquad (54)$$

(iii) *Difference of the Specific Heats.*

Since

$$dS = c_v dT + b dv,$$

$$= c_p dT + b'dp,$$

we have

$$(c_p - c_v)dT = bdv - b'dp,$$

or

$$c_p - c_v = b\left(\frac{dv}{dT}\right)_p,$$

by putting $dp = 0$.

Substituting for b from equation (50), this becomes:

$$c_p - c_v = T\left(\frac{dp}{dT}\right)_v \cdot \left(\frac{dv}{dT}\right)_p. \quad . \quad . \quad . \quad (55)$$

Now by equation (10):

$$\left(\frac{dp}{dT}\right)_v = -\left(\frac{dp}{dv}\right)_T \cdot \left(\frac{dv}{dT}\right)_p.$$

Hence by substitution in equation (55):

$$c_p - c_v = -T\left(\frac{dp}{dv}\right)_T \left(\frac{dv}{dT}\right)_p^2. \quad . \quad . \quad . \quad (56)$$

For all known substances at constant temperature increase of pressure leads to decrease of volume, and therefore $\left(\frac{dp}{dv}\right)_T$ is always negative. That is, $c_p - c_v$ is positive, or the specific heat at constant pressure is never less than the specific heat at constant volume.

When the coefficient of expansion of a substance is zero, at the maximum density for instance, $\left(\frac{dv}{dT}\right)_p = 0$, and from equation (55):

$$c_p = c_v.$$

This occurs in the case of water at approximately 4° C.

Equation (56) can be written in a form which enables the difference in the specific heats to be calculated from well-known physical constants.

The coefficient of expansion of a substance at constant pressure is defined by the equation:

$$a = \frac{1}{v}\left(\frac{dv}{dT}\right)_p,$$

and the bulk modulus of elasticity by:

$$K = -v\left(\frac{dp}{dv}\right)_T.$$

Substituting in (56):

$$c_p - c_v = Kv\alpha^2 T \quad . \quad . \quad . \quad . \quad . \quad (57)$$

41. Numerical Example.—When the specific heat of a body is measured by an ordinary calorimetric method it is the specific heat at constant pressure that is really measured, as the substance is free to expand. Various theoretical formulæ have been devised to show the variation of specific heat of solids with temperature, and these relate to the specific heat at constant volume. From the measured value of c_p the value of c_v can be found by the use of equation (57).

As an example we shall take the case of copper at 0° C. From experiment it is found:

$$c_p = 0\cdot0909 \text{ calorie per degree C.}$$

$$a = 50\cdot1 \times 10^{-6} \text{ per degree C.}$$

$$K = 1\cdot85 \times 10^{12} \text{ dynes per sq. cm.}$$

$$v = 0\cdot112 \text{ ccs.}$$

Hence

$$\begin{aligned} c_p - c_v &= Kv\alpha^2\mathrm{T} \\ &= \frac{1\cdot85 \times 10^{12} \times 0\cdot112 \times (50\cdot1)^2 \times 10^{-12} \times 273\cdot1}{4\cdot185 \times 10^7} \\ &= 0\cdot0034 \end{aligned}$$

Therefore

$$c_v = 0\cdot0875 \text{ calorie per degree C.}$$

42. Case of a Perfect Gas.—From equation (56) we can calculate the difference in the specific heats of a perfect gas.

In this case we have:

$$pv = RT.$$

Hence

$$\left(\frac{dv}{dT}\right)_p = \frac{R}{p},$$

and

$$\left(\frac{dp}{dv}\right)_T = -\frac{p}{v}.$$

Therefore

$$c_p - c_v = \frac{R^2}{p^2} \cdot \frac{p}{v} \cdot T = R,$$

the same result as obtained previously.

CHAPTER V

THE ABSOLUTE SCALE OF TEMPERATURE

43. The Joule-Thomson Porous Plug Experiment.—It has been explained in Chapter II how Joule tested the hypothesis that the internal energy of a gas is a function of the temperature only. The reason that no change in temperature was detected in these experiments was due to the large thermal capacity of the apparatus as compared with that of the gas. To detect the thermal effects which might reasonably have been expected a much more sensitive method than the one employed would have been necessary. A more sensitive method of testing the hypothesis was devised later in conjunction with Thomson (Lord Kelvin), experiments being performed with great care over the period 1852 to 1862.*

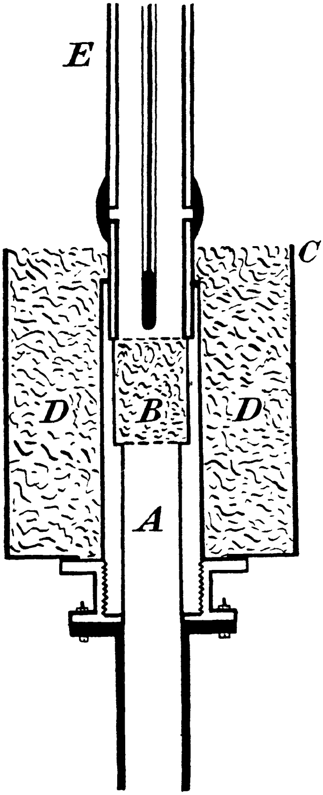

Fig. 19.
The Porous Plug Experiment.

The experimental procedure in this more delicate method was to force the gas under examination at a slow uniform rate through a porous plug and observe the rise or fall in temperature of the issuing gas. Fig. 19 shows the general arrangement of the apparatus. The gas circulated through a long spiral copper tube immersed in a constant-temperature bath which raised the temperature of the gas to any desired level. This temperature was measured with a mercury thermometer. The gas then came up the tube A and passed through a porous plug B. Cotton-wool was used for low-pressure differences and compressed silk for high-pressure differences, the plug being secured in position in a short boxwood tube by means of two perforated brass discs. A cylindrical tin jacket C surrounded the boxwood tube, the space being packed with cotton-wool, D, to prevent conduction of heat from the bath. A thermometer was suspended at a short distance above the plug to take the temperature of the issuing gas, the tube E being of glass to permit the reading of the thermometer. The initial pressure of the gas was measured by a gauge attached to the copper spiral, the final pressure being that of the atmosphere.

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* *Phil. Mag.*, 4th ser., **4** (1852); *Phil. Trans. Roy. Soc* (1853), (1854), (1862).

Slight modifications were made in the apparatus for use with gases such as hydrogen, which could only be obtained in limited quantities, but in essentials it remained the same as when used for air and carbon dioxide, and described above.

For all the gases examined it was found that there was a thermal effect in passing through the plug; air, oxygen, and carbon dioxide exhibited a cooling effect, but hydrogen issued at a slightly higher temperature than that of the bath.

The conditions of the experiment are such that there is no change in kinetic energy, the gas issuing in small eddies which rapidly subside, no external work is performed and there is no external loss of heat. In these circumstances we have already seen that the equation of steady flow (41) reduces to the form:

$$H_1 = H_2,$$

or

$$E_1 + p_1v_1 = E_2 + p_2v_2.$$

If the gas under consideration obeys Boyle's law accurately the produce pv is unchanged and therefore $E_1 = E_2$, and the temperature of the gas will be unaltered by its passage through the plug if the internal energy is a function of the temperature only. *Mutatis mutandis*, if the temperature of the gas is found to be the same on either side of the plug and the gas obeys Boyle's law the internal energy must be a function of the temperature only. This experiment gives a more delicate test of Mayer's hypothesis than Joule's original experiments, as the thermal capacity of the apparatus has no effect upon the change in temperature.

No known gas, however, obeys Boyle's law accurately, the product pv decreasing with increase of pressure for most gases up to a certain limit, as shown by the experiments of Amagat and others. Hence in the majority of cases pv will be less on the high-pressure side, and the internal energy on the low-pressure side of the plug will be less by an amount

$$E_1 - E_2 = p_2v_2 - p_1 v_1,$$

which would result in a cooling effect even if Mayer's hypothesis were true.

Any molecular attraction in the gas will result in a cooling on free expansion—or expansion without doing external work—as the energy necessary to separate the molecules still farther from one another must come from the store of energy in the gas, i.e. its internal energy. In the case of hydrogen and like substances for which the product pv increases with pressure, a slight heating effect would be expected if Mayer's hypothesis were true. The effect of inter-molecular attractions might be sufficient to reduce considerably this rise of temperature, and in some cases to overcome it and produce a cooling effect.

From the foregoing it will be seen that the observed heating or cooling effect is the sum of the effects arising from two quite distinct causes. If the deviations from Boyle's law are small, they will in some cases lie outside the limits of experimental error, and in this case the whole effect may be attributed to the expansion under molecular forces, and will consequently be a measure of the deviation from Mayer's hypothesis.

44. Theory of the Method.—Combining equations (34) and (40) we have for any small transformation:

$$dH = TdS + vdp, \quad . \quad . \quad . \quad . \quad . \quad (58)$$

and as this is a transformation at constant total heat:

$$0 = TdS + vdp. \quad . \quad . \quad . \quad . \quad . \quad (59)$$

The entropy is a function of any two variables which define the state of the substance, and hence

$$\begin{aligned} dS &= \left(\frac{dS}{dp}\right)_T dp + \left(\frac{dS}{dT}\right)_p dT, \\ &= -\left(\frac{dv}{dT}\right)_p dp + \left(\frac{dS}{dT}\right)_p dT \end{aligned}$$

by the fourth thermodynamic relation.

Therefore (59) becomes:

$$vdp - T.\left\{\left(\frac{dv}{dT}\right)_p dp - \left(\frac{dS}{dT}\right)_p dT\right\} = 0,$$

or

$$c_p\left(\frac{dT}{dp}\right)_H = T\left(\frac{dv}{dT}\right)_p - v,$$

as

$$T\left(\frac{dS}{dT}\right)_p = \left(\frac{\delta q}{dT}\right)_p = c_p.$$

The quantity $\left(\frac{dT}{dp}\right)_H$ is a measure of the "cooling effect," and will be written μ.

Hence

$$c_p\mu = T\left(\frac{dv}{dT}\right)_p - v, \quad . \quad . \quad . \quad . \quad . \quad (60)$$

The contributions made to the cooling effect by the deviations from Boyle's law and Mayer's hypothesis can be analysed mathematically.

$$H = E + pv,$$

or

$$dH = dE + pdv + vdp.$$

Hence

$$\left(\frac{dH}{dp}\right)_T = \left(\frac{dE}{dp}\right)_T + p\left(\frac{dv}{dp}\right)_T + v. \quad . \quad . \quad . \quad . \quad (61)$$

But

$$dE = TdS - pdv.$$

and hence

$$\left(\frac{dE}{dp}\right)_T = T\left(\frac{dS}{dp}\right)_T - p\left(\frac{dv}{dp}\right)_T,$$

$$= - T\left(\frac{dv}{dT}\right)_p - p\left(\frac{dv}{dp}\right)_T,$$

by the fourth thermodynamic relation.

Substitution in equation (61) gives:

$$\left(\frac{dH}{dp}\right)_T = v - T\left(\frac{dv}{dT}\right)_p,$$

whence, on comparison with equation (60):

$$c_p\mu = -\left(\frac{dH}{dp}\right)_T. \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

But

$$\left(\frac{dH}{dp}\right)_T = \left(\frac{dE}{dp}\right)_T + \left(\frac{d(pv)}{dp}\right)_T.$$

Therefore

$$c_p\mu = -\left(\frac{dE}{dp}\right)_T - \left(\frac{d(pv)}{dp}\right)_T.$$

The first term on the right-hand side represents the departure from Mayer's hypothesis, and the second that from Boyle's law. The quantity $\left(\frac{dE}{dp}\right)_T$ is always negative for a gas because the potential energy of the attractive forces between the molecules is diminished by decreasing the volume or by increasing the pressure. This term will always therefore represent a cooling effect, whereas the term $\left(\frac{d(pv)}{dp}\right)_T$ may be a cooling or heating effect.

45. Formation of Characteristic Equations.—The equation (60) for the cooling effect can be integrated if μ is known as a function of the other variables, and will then give a characteristic equation for the particular gas.

From their experiments upon air and carbon dioxide, Joule and Thomson concluded that μ varied inversely as the square of the absolute temperature.

That is:

$$\mu = \frac{k}{T^2}.$$

Substituting in (60):

$$\frac{kc_p}{T^2} = T\left(\frac{dv}{dT}\right)_p - v$$

or

$$\frac{kc_p}{T^4} = \frac{d}{dT}\left(\frac{v}{T}\right)_p.$$

Integrating this equation, assuming c_p constant:

$$-\frac{kc_p}{3T^3}=\frac{v}{T}+f(p). \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

In this equation $f(p)$ is some function of the pressure and occurs because the differentiation is performed at constant pressure when this function will disappear.

At high temperatures the gas will approximate in behaviour to a perfect gas for which $pv = RT$. The term $-\frac{kc_p}{3T^3}$ in (62) will be small at high temperatures, and will be negligible in comparison with the other terms. Consequently it follows that

$$f(p) = -\frac{R}{p},$$

or substituting in equation (63):

$$pv = RT - \frac{kc_p p}{3T^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (64)$$

This equation was deduced by Joule and Thomson, and is similar to an equation previously obtained by Rankine to represent Regnault's results for carbon dioxide. The equation, as it stands, is open to the objection that it does not give the negative cooling effect for gases such as hydrogen. It is now known that most gases display a negative cooling effect if the temperature of the experiment is sufficiently high. Consequently there must be one temperature at which the cooling effect disappears. This is known as the "inversion" temperature for the cooling effect, and ordinary air temperatures such as were used in the original experiments are well above the inversion temperature for hydrogen.*

The equation (63) when modified by replacing v by $(v - b)$, where b is a constant and probably represents the volume occupied by the molecules,† satisfactorily accounts for this inversion of the cooling effect. Thus:

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* Temperature of inversion for hydrogen is − 80·5° C. Olszewski, *Nature*, **65**, 572 (1902).

† See Callendar, *Properties of Steam*, p. 57; also *Proc. Roy. Soc.*, A., **120**, 460 (1928).

$$v - b = \frac{RT}{p} - \frac{kc_p}{3T^2}, \quad . \quad . \quad . \quad . \quad . \quad (65)$$

and on differentiation and substitution in equation (60):

$$c_p\mu = \frac{kc_p}{T^2} - b, \quad . \quad . \quad . \quad . \quad . \quad . \quad (66)$$

from which it will be seen that μ can be positive or negative according to the relative magnitudes of the quantities on the right-hand side.

The original method of deducing equation (60) is actually inadmissible, as the assumption of $\mu = \frac{k}{T^2}$ is inconsistent with c_p constant. This may be shown as follows.

We have already seen equation (62) that

$$c_p\mu = -\left(\frac{dH}{dp}\right)_T,$$

and hence, as dH can be expressed in the form:

$$dH = \left(\frac{dH}{dT}\right)_p dT + \left(\frac{dH}{dp}\right)_T dp,$$

we have by substitution from equations (53) and (62):

$$dH = c_p dT - c_p\mu dp.$$

Now as dH is a complete differential:

$$\left(\frac{dc_p}{dp}\right)_T = -\left(\frac{d(c_p\mu)}{dT}\right)_p,$$

or with our former assumptions:

$$0 = \frac{2c_p k}{T^3},$$

which is only possible when k is zero, i.e. in a perfect gas for which the equation $pv = RT$ is true.

This inconsistency can be avoided if it is assumed that the product $c_p\mu$ varies inversely as T^n.

On substituting in equation (60), integrating and replacing v by $(v - b)$ as before, we have:

$$v - b = \frac{RT}{p} - c, \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

where c varies inversely as T^n.

This equation is similar to (65) in that it gives positive or negative values for the cooling effect depending upon the value of T. It was deduced by Callendar for an imperfect gas or a saturated vapour, and has been of great use in computing thermodynamically consistent tables of the properties of steam. Unlike the equations proposed by Van der Waals and others, it is not intended to represent the liquid state of a fluid.

46. The Temperature of Melting Ice on the Thermodynamic Scale and the Corrections to a Gas Thermometer.—When considering a Carnot cycle for a perfect gas we saw that the temperature on the gas scale in this case agreed with the temperature on the absolute thermodynamic scale. No known gas behaves exactly as a perfect gas, and as gas thermometers are used to realise an absolute scale, it is important that the necessary corrections to be applied to the readings of such a thermometer should be known accurately.

The Joule-Thomson experiment gives us a method of calculating these corrections, and also of obtaining the temperature of melting ice on the thermodynamic scale.

The Joule-Thomson effect as given by equation (60) is:

$$c_p\mu = T\left(\frac{dv}{dT}\right)_p - v,$$

in which T refers to the absolute thermodynamic temperature. Suppose we have an air thermometer, with which all our temperature measurements have to be made, and we require to find the connection between the indications of this thermometer and the absolute thermodynamic scale. The only quantities in equation (60) which can be measured absolutely are v and p and changes in these quantities.

Let θ be the reading of the gas thermometer corresponding to the absolute temperature T; then as T must be some function of θ we can write:

$$\left(\frac{dv}{dT}\right)_p = \left(\frac{dv}{d\theta}\cdot\frac{d\theta}{dT}\right)_p,$$

and

$$c_p = \left(\frac{\delta q}{dT}\right)_p = \left(\frac{\delta q}{d\theta}\cdot\frac{d\theta}{dT}\right)_p = c'_p\,\frac{d\theta}{dT}.$$

Substituting these values in equation (60), this becomes:

$$c'_p\,\frac{d\theta}{dT}\left(\frac{dT}{d\theta}\cdot\frac{d\theta}{dp}\right) = T\left(\frac{dv}{d\theta}\right)_p\cdot\frac{d\theta}{dT} - v,$$

or

$$c'_p\,\frac{d\theta}{dp} + v = T\left(\frac{dv}{d\theta}\right)_p\cdot\frac{d\theta}{dT}.$$

Therefore

$$\int_{T_1}^{T_2}\frac{dT}{T} = \int_{\theta_1}^{\theta_2}\left\{\left(\frac{dv}{d\theta}\right)_p d\theta\right\}\bigg/\left\{c'_p\,\frac{d\theta}{dp} + v\right\},$$

or

$$\log\frac{T_2}{T_1} = \int_{\theta_1}^{\theta_2}\left\{\left(\frac{dv}{d\theta}\right)_p d\theta\right\}\bigg/\left\{c'_p\,\frac{d\theta}{dp} + v\right\}, \quad . \quad . \quad (68)$$

Now $\frac{1}{v}\left(\frac{dv}{d\theta}\right)_p$ is the coefficient of expansion of air as observed by the air thermometer, and $\frac{d\theta}{dp}$ and c'_p the cooling effect, and specific heat both as observed by the same thermometer.

The interval of temperature between the melting-point of ice and the boiling-point of water is defined as 100 degrees. Consequently we can rewrite equation (68) in the form:

$$\log\frac{T_0 + 100}{T_0} = \int_{\theta_0}^{\theta_0 + 100}\left\{\left(\frac{dv}{d\theta}\right)_p d\theta\right\}\bigg/\left\{c'_p\,\frac{d\theta}{dp} + v\right\}, \quad . \quad (69)$$

where T_0 and θ_0 are the values of the ice point temperature on the thermodynamic and gas scales respectively. From equation (69) the value of T_0 can be found from measurements of the thermal properties of air between the melting-point of ice and the boiling-point of water.

Having found T_0, the value of any temperature T can be found from equation (68), provided the properties of air are known over the range T_0 to T.

47. Callendar's Method.—Equations (68) and (69) would be extremely inconvenient in practice for the calculation of the ice point and the corrections to the gas thermometer scale, as the right-hand side would have to be integrated graphically or by a method involving laborious calculation.

Callendar* has proposed a method which enables the corrections to be obtained with a minimum of calculation.

The characteristic equation for a gas can be written:

$$T = \frac{pv}{R} + a, \quad . \quad . \quad . \quad . \quad . \quad . \quad (70)$$

where a replaces $\frac{p}{R}(c - b)$ of equation (67).

The temperature indicated by a gas thermometer is given by:

$$\theta = \frac{pv}{R_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (71)$$

where R_1 is a constant differing slightly in value from R.

If T_0 and T_1 and letters similarly suffixed denote the ice point and steam point respectively, we have:

$$\left.\begin{aligned} T_1 &= \frac{p_1v_1}{R} + a_1, & T_0 &= \frac{p_0v_0}{R} + a_0 \\ \theta_1 &= \frac{p_1v_1}{R_1}, & \theta_0 &= \frac{p_0v_0}{R_1} \end{aligned}\right\}, \quad . \quad . \quad . \quad (72)$$

Solving for R and R_1 and remembering that:

$$T_1 - T_0 = \theta_1 - \theta_0 = 100,$$

$$R_1 = R\left(1 + \frac{a_0 - a_1}{100}\right) = \frac{p_1v_1 - p_0v_0}{100} \quad . \quad . \quad (73)$$

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* Callendar, *Phil. Mag.*, 5, 48 (1903).

By equations (72) the correction to the gas thermometer at the ice point is given by:

$$T_0 - \theta_0 = a_0 + p_0v_0\left(\frac{1}{R} - \frac{1}{R_1}\right),$$

but by equation (73):

$$\frac{1}{R} - \frac{1}{R_1} = \frac{1}{R_1} \cdot \frac{a_0 - a_1}{100}.$$

Hence

$$T_0 - \theta_0 = a_0 + \frac{a_0 - a_1}{100} \cdot \theta_0. \quad . \quad . \quad . \quad (74)$$

Again, if t is the temperature Centigrade, and Δt the correction to be applied, we have:

$$t = \theta - \theta_0,$$

and

$$\Delta t = (T - T_0) - (\theta - \theta_0)$$
$$= (pv - p_0v_0)\left(\frac{1}{R} - \frac{1}{R_1}\right) + a - a_0,$$

or using equations (72) and (73):

$$\Delta t = \frac{a_0 - a_1}{100} \cdot t - (a_0 - a). \quad . \quad . \quad . \quad . \quad (75)$$

Using Callendar's equation in the form (67), equation (60) for the cooling effect becomes:

$$c_p\,\mu = (n + 1)\,c - b, \quad . \quad . \quad . \quad . \quad (76)$$

and also by differentiating (67):

$$\left(\frac{d\,(pv)}{dp}\right)_T = -\,(c - b). \quad . \quad . \quad . \quad . \quad (77)$$

Now, as

$$a = \frac{p}{R}\,(c - b), \quad . \quad . \quad . \quad . \quad . \quad . \quad (78)$$

equations (77) and (78) used in conjunction with (75) would enable the value of Δt to be calculated at any temperature; as the corrections to be applied are small, however, uncertainty is introduced by using compressibility curves alone as would be required by equation (77). By using equations (76) and (77) combined a more accurate method is available.

We shall limit the rest of our investigation to a constant-volume gas thermometer which is filled with a diatomic gas such as hydrogen, oxygen, or nitrogen.

As a first approximation we have

$$p = p_0 \frac{T}{T_0},$$

the volume being supposed constant, and

$$c = c_0 \left(\frac{T_0}{T}\right)^n.$$

Substituting these values in equation (78), we have

$$a = \frac{p_0 c_0}{R} \left(\frac{T_0}{T}\right)^{n-1} - \frac{p_0 b T}{R T_0},$$

and

$$a_0 = \frac{p_0 c_0}{R} - \frac{p_0 b}{R}.$$

Substituting these values in equations (74) and (75) we have:

$$T_0 - \theta_0 = \frac{p_0 c_0}{R}\left\{1 + \frac{273}{100}\left(1 - \left(\frac{273}{373}\right)^{n-1}\right)\right\} \quad . \quad . \quad (79)$$

and

$$\Delta t = \frac{p_0 c_0}{R}\left\{\left(1 - \left(\frac{273}{373}\right)^{n-1}\right)\frac{t}{100} - \left(1 - \left(\frac{273}{T}\right)^{n-1}\right)\right\}, \quad . \quad (80)$$

where T_0 and θ_0 have been replaced by 273, and T_1 by 373 on the right-hand side, which is sufficiently accurate as the expressions are in both cases only small correction terms.

From equation (79) and the data for hydrogen Callendar obtains the value 273·1° as the absolute thermodynamic temperature of the ice point, taking the value of n as 1·5.

Equation (80) is used to calculate a table of corrections for the constant-volume gas thermometer. The table for a constant-volume hydrogen thermometer, the initial pressure being one metre of mercury, is given below.

TABLE IV.

Temperature, °C.	Correction.	Temperature, °C.	Correction.	Temperature, °C.	Correction.
− 250	+ 0·1005	10	− 0·00016	80	− 0·00024
− 200	+ 0·0311	20	− 0·00028	90	− 0·00013
− 150	+ 0·0132	30	− 0·00036	150	+ 0·00097
− 100	+ 0·0054	40	− 0·00040	200	+ 0·00236
− 50	+ 0·00164	50	− 0·00040	300	+ 0·0059
− 20	+ 0·00048	60	− 0·00038	450	+ 0·0127
− 10	+ 0·00021	70	− 0·00032	1,000	+ 0·0438

48. Hoxton's Method.—A more direct method for obtaining the ice point and the gas scale corrections has been devised by Buckingham* and used by Hoxton.†

The equation for the cooling effect is:

$$c_p\mu = T\left(\frac{dv}{dT}\right)_p - v, \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

which can be written in the form:

$$\frac{d}{dT}\left(\frac{v}{T}\right) = \frac{\mu c_p}{T^2},$$

and hence

$$\int_{T_0}^{T} d\left(\frac{v}{T}\right) = \int_{T_0}^{T} \frac{\mu c_p}{T^2} dT,$$

where T_0 is the temperature of melting ice on the absolute scale. Performing the integration we have:

$$\frac{v}{T} - \frac{v_0}{T_0} = \int_{T_0}^{T} \frac{\mu c_p}{T^2} dT.$$

But

$$v = v_0(1 + at),$$

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* Buckingham, *Bull. Bur. Stds.*, **3**, 237 (1907).

† Hoxton, *Phys. Rev.*, **13**, 438 (1919).

where a is the coefficient of expansion of the gas at constant pressure, and t is the Centigrade temperature on the gas scale we are considering.

Therefore

$$\frac{v_0(1 + at)}{T} - \frac{v_0}{T_0} = \int_{T_0}^{T} \frac{\mu c_p}{T^2} dT. \quad . \quad . \quad . \quad (81)$$

The integral on the right-hand side of this equation can be evaluated if the variation of μ and c_p with temperature are known. Hoxton gives the equation

$$\mu = -0\cdot2599 + 182\cdot0 \, . \, \frac{1}{T} - 552\cdot4 \frac{p}{T^2} \quad . \quad . \quad (82)$$

to express the variation of μ with pressure and temperature in the case of air, where p is in metres of mercury and $T = 273 + t$.

If, now, an average value of c_p is evaluated for the range T_0 to T, equation (81) can be integrated and becomes:

$$\frac{v_0(1 + at)}{T} - \frac{v_0}{T_0} = \bar{c}_p(M - M_0), \quad . \quad . \quad . \quad (83)$$

where

$$(M - M_0) = \int_{T_0}^{T} \frac{\mu}{T^2} dT,$$

and $\bar{c}_p$ is the average value of c_p over the range of temperature considered. Since v_0 is the specific volume we can put

$$v_0 = \frac{1}{\rho_0},$$

where ρ_0 is the density at 0 °C. and equation (83) reduces to

$$T_0(1 + at) - T = TT_0\rho_0\bar{c}_p(M - M_0). \quad . \quad . \quad (84)$$

If it is required to find the ice point on the thermodynamic scale we consider the range of temperature between the ice and steam points. In this case

$$T = T_0 + 100,$$
$$t = 100,$$

as the temperature interval is defined as 100 degrees.

Equation (84) then becomes:

$$T_0 = \frac{1}{a} + \frac{T_0(T_0 + 100)}{100a} \rho_0 \bar{c}_p (M_{100} - M_0). \quad . \quad . \quad (85)$$

The first term on the right-hand side of this equation is the temperature of the ice point on the scale defined by the gas being considered. The second term is the quantity which must be added thereto to derive the temperature of the same fixed point on the thermodynamic scale. This will be small in comparison with the first term and can be called the "correction".

The accuracy of the correction term is limited by the accuracy of the determination of μ, which in Hoxton's experiments was about one per cent. As the correction is roughly one degree the accuracy will be about 0·01° C. Two approximations are therefore permissible; T_0 may be replaced by 273 in the correction term, and in the evaluation of the integral

$$\int_{T_0}^{T_0 + 100} \frac{\mu}{T^2} dT;$$

using equation (82) for μ, T can be taken to be $273 + t$. With these approximations equation (85) becomes:

$$T_0 = \frac{1}{a} + \frac{273 \times 373}{100a} \rho_0 \bar{c}_p \, (M_{100} - M_0) \quad . \quad . \quad (86)$$

The value of $(M_{100} - M_0)$ as computed by Hoxton is $+ 0{\cdot}000306$, and substituting this value and the appropriate values for the quantities in (86) he obtains 273·36° as the temperature of melting ice on the thermodynamic scale, which is rather higher than Callendar's value, and that given by Birge,[*] namely 273·18°.

In order to calculate the corrections to the gas thermometer scale we put in equation (84):

$$T - T_0 = t_a,$$

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[*] Birge, *Phys. Rev. Supplement*, **1**, 1 (1929). This paper contains a useful summary of the most recent work.

where t_a is the Centigrade temperature on the absolute thermodynamic scale, and

$$T_0 = \frac{1}{a} + \eta,$$

where η is the correction term of equation (85).

Making these substitutions (84) becomes:

$$-t_a + t + a\eta t = TT_0 \rho_0 \bar{c}_p (M - M_0),$$

or

$$t_a - t = a\eta t - TT_0 \rho_0 \bar{c}_p (M - M_0), \quad . \quad . \quad (87)$$

in which $t_a - t$ is the correction sought.

Replacing η by the correction term from equation (86) and replacing T_0 and $\frac{1}{a}$ by 273, equation (87) now becomes:

$$t_a - t = 273\, \rho_0 \bar{c}_p \{3 \cdot 73 (M_{100} - M_0) t - (M - M_0)(273 + t)\}.$$

It will be noticed that the correction given by this equation is zero at the ice and steam points, where both scales are made to agree by definition. The corrections to the air thermometer scale as calculated by Hoxton are in good agreement with the average values of other observers.

CHAPTER VI

EQUATIONS OF STATE

49. Kinetic Theory.—It was pointed out in Chapter I that no known gas accurately obeys the law $pv = RT$, although the behaviour of gases at high temperatures and low pressures approximates closely to that of a perfect gas. A number of other equations of state have been proposed to represent the experimental results with greater accuracy. Some of these equations, such as that of Van der Waals, are attempts to represent in one equation the properties of both the gas and the liquid; others deal only with a restricted range of conditions, and accuracy over a definite range rather than comprehensiveness is the aim of these. No equation so far proposed can be considered as a final solution of the problem, but the equations are useful for certain purposes.

By making assumptions regarding the behaviour of the molecules of a gas we can deduce equations of state whose validity will depend upon how far the assumptions made can be regarded as an approximation to the truth for the particular gas.

The most simple assumptions that can be made with regard to the molecules of a gas are that all the molecules are alike, infinitely small rigid spheres, moving about in all directions, and the volume of the spheres is negligible in comparison with the volume occupied by the gas. Also it must be assumed that the time occupied in a collision between the molecules themselves or a molecule and the walls of the containing vessel is zero. This is equivalent to the assumption that the molecules exert no attractive or repulsive forces on each other.

Suppose the gas to be contained in a rectangular box of unit volume, the sides of which lie along the axes x, y, z. The pressure of the gas is due to the impacts of the molecules upon the walls of the containing vessel, and is equal to the rate of change of momentum over unit area. Consider any molecule in the gas moving with a velocity the components of which along the three axes are u, v, w. When this molecule impinges on the face normal to the x axis it will move off again with its velocity along the x axis reversed, i.e. the components of its velocity will be $-u$, v, w, and the impulse on the wall is $2mu$, if m is the mass of the molecule. If there are n molecules with velocities u, v, w, the number of molecules in this group impinging on an area dS perpendicular to the x axis in time dt is:

$$nudSdt.$$

The impulse communicated to the area in this time is:

$$nudSdt \times 2mu = 2mnu^2dSdt,$$

or the pressure produced by this group of molecules is:

$$2mnu^2.$$

The total pressure produced by all the molecules is obtained by summing this expression for all positive values of u. Denoting the pressure by p we have:

$$p = \Sigma 2mnu^2 = 2m\Sigma nu^2 = mN\overline{u^2},$$

where N is the total number of molecules present and $\overline{u^2}$ is the mean square velocity along the x axis, the factor 2 having disappeared as the summation extends only over positive values of u.

By considering the faces perpendicular to the axes of y and z similar results are obtained, and as the pressure is the same throughout the gas this can be expressed by the relations:

$$p = mN\overline{u^2} = mN\overline{v^2} = mN\overline{w^2},$$

or

$$3p = mN\{\overline{u^2} + \overline{v^2} + \overline{w^2}\}.$$

Putting

$$\overline{V^2} = \overline{u^2} + \overline{v^2} + \overline{w^2},$$

where $\overline{V^2}$ is the mean square velocity, we have:

$$p = \tfrac{1}{3}mN\overline{V^2}.$$

As N is the number of molecules in unit volume and m the mass of each molecule, mN is the mass per unit volume $= \rho$, the density.

Hence

$$p = \tfrac{1}{3}\rho\overline{V^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (88)$$

The reciprocal of the density is the volume per unit mass, so for unit mass of gas equation (88) becomes:

$$pv = \tfrac{1}{3}\overline{V^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (89)$$

From the empirical law $pv = RT$ we see by comparison with equation (89) that

$$RT = \tfrac{1}{3}\overline{V^2},$$

or the kinetic energy of the molecules is:

$$\tfrac{3}{2}RT.$$

Assuming that the mean square velocity of the molecules is proportional to the absolute temperature, equation (89) may be written in the familiar form:

$$pv = RT,$$

which is the equation of state for any gas for which all the assumptions made are true. As it is known that this law is not obeyed under all conditions, it is necessary to examine our assumptions and modify them to obtain a more accurate equation.

50. Van der Waals' Equation.—Van der Waals' equation may be written:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT, \quad . \quad . \quad . \quad . \quad (90)$$

where a and b are constants for the particular fluid and R is the gas constant.

This equation was proposed in 1873 for the gaseous and liquid states of a fluid, and accounts qualitatively for many important properties, but quantitatively it fails in many particulars.

The characteristic equation for a perfect gas was obtained by neglecting the finite size of the molecules. If this be taken into account it is obvious that the equation must be modified, for the distance traversed by a molecule between two successive encounters will be less than if the molecules were point spheres. Let the average distance traversed by a molecule between two successive encounters be denoted by λ, the mean free path. In Fig. 20 suppose A and B to be two molecules of diameter d at a distance λ apart. If these molecules were to impinge along the line of centres the path moved over would be less by an amount d than if the molecules were point spheres. Now all the encounters between molecules are not direct, so their mean free paths will not all be lessened by d, but on the average the path will be lessened by an amount kd where k is a fraction. That is, the mean free path is diminished in the ratio $(\lambda - kd) : \lambda$, or $\left(1 - \frac{kd}{\lambda}\right) : 1$.

If the mean free path is lessened in this ratio, the encounters per second will be increased in the ratio $1 : 1 - \frac{kd}{\lambda}$. But the pressure of the gas depends upon the encounters per second with the wall of the containing vessel. Hence the new pressure is given by:

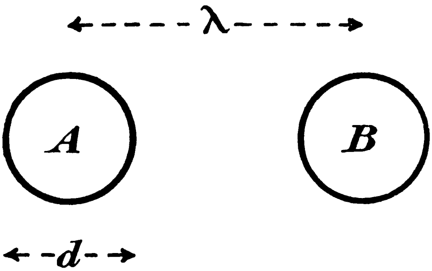

FIG. 20.

$$p = \frac{1}{3}\rho\overline{V}^2 \cdot \frac{1}{1 - \frac{kd}{\lambda}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (91)$$

The mean free path is inversely proportional to the density of the gas, for if the volume were halved, i.e. the density doubled, there would be twice as many molecules in the same space, and therefore any molecule would only have to travel approximately half as far before encountering another molecule. Hence writing v for $\frac{1}{\rho}$ and $\frac{b}{v}$ for $\frac{kd}{\lambda}$ in equation (91), we have:

$$pv\left(1 - \frac{b}{v}\right) = \frac{\overline{V^2}}{3} = RT,$$

or $$p\,(v - b) = RT. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (92)$$

Next consider the forces of cohesion which act between a molecule and those surrounding it. When the molecule is sufficiently far removed from the surface of the gas all directions for the resultant of these cohesive forces are equally probable, as the individual forces are varying continuously as the surrounding molecules change their positions. Hence if the resultant is averaged over a sufficient length of time the aggregate force will be nil. This is not true, however, when the molecule is near the surface. Let the force from each molecule be resolved into normal and tangential components. All directions for the resultant in the tangential plane are equally likely, but the resultant normal component is most often directed inwards. Averaged over a sufficient length of time the total resultant force will therefore be a normal force always directed inwards. Thus the average effect of the cohesive forces is the same as if there was a permanent field of force acting at and near the surface. This field of force can be regarded as exerting a pressure p_1 over the boundary of the gas. The pressure is proportional to the number of molecules per unit area near the boundary surface and to the normal component of the force. Both of these factors are proportional to the density, so p_1 will be proportional to the square of the density. That is:

$$p_1 = a\rho^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (93)$$

where a is a constant.

Hence the molecules are not deflected by impact alone on reaching the boundary, but as the total result of their impact and of the action of the supposed field of force. That is, their change of momentum may be supposed to be produced by a total pressure $p + p_1$ instead of by the simple pressure p.

Hence equation (92) now becomes:

$$(p + p_1)\,(v - b) = RT,$$

or $$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

by substitution for p_1 from (93) and replacing ρ^2 by $\frac{1}{v^2}$.

51. Critical Constants.—The general form of the isothermals for carbon dioxide given by Van der Waals' equation is shown in Fig. 21. These curves are obtained from the equation:*

$$\left(p + \frac{0 \cdot 00874}{v^2}\right)(v - 0 \cdot 0023) = \frac{1 \cdot 00646}{273} T., \quad . \quad (94)$$

where the unit of pressure is the atmosphere, and the unit of volume that of the gas at 0° C. under one atmosphere pressure.

By comparison with Fig. 3 it will be seen that for the isothermals above the critical temperature the shape is similar to that found experimentally by Andrews; but below the critical temperature there are changes in curvature and three values of v for certain values of p, a horizontal portion corresponding to liquefaction not being given by the equation.

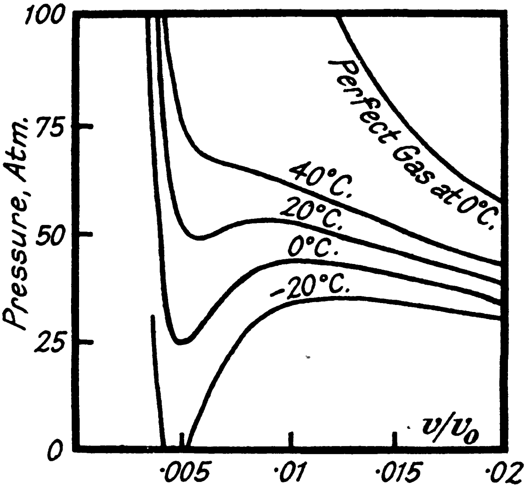

Fig. 21.

Van der Waals' Isothermals for Carbon Dioxide.

Van der Waals' equation being a cubic in v has three roots which may be either all real, or two imaginary and one real, as imaginary roots always occur in pairs. In Fig. 21 the 40° C. isothermal corresponds to the first condition, and the other isothermals to the latter. There is one isothermal where there are three real coincident roots at a point of inflexion. All the isothermals for temperatures higher than that corresponding to the isothermal with three real coincident roots have no horizontal tangent, and all those lower have a maximum and minimum. Consequently this curve is identified with the critical isothermal. The temperature of the critical isothermal is obtained in the following manner. Equation (90) may be written:

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* Numerical values obtained from Regnault's results.

$$v^3 - \left(b + \frac{RT}{p}\right)v^2 + \frac{av}{p} - \frac{ab}{p} = 0. \quad . \quad . \quad (95)$$

Now at the critical point, as the three roots are equal, the equation must be of the form:

$$(v - v_c)^3 = 0. \quad . \quad . \quad . \quad . \quad . \quad (96)$$

where the suffix *c* denotes conditions at the critical point. For the critical point equation (95) becomes:

$$v^3 - \left(b + \frac{RT_c}{p_c}\right)v^2 + \frac{av}{p_c} - \frac{ab}{p_c} = 0. \quad . \quad . \quad (97)$$

Equations (96) and (97) are identical, hence equating coefficients

$$3v_c = b + \frac{RT_c}{p_c},$$

$$3v_c^2 = \frac{a}{p_c},$$

$$v_c^3 = \frac{ab}{p_c},$$

and from these by a simple reduction we have:

$$\left.\begin{aligned} v_c &= 3b \\ p_c &= \frac{a}{27b^2} \\ T_c &= \frac{8}{27} \cdot \frac{a}{bR} \end{aligned}\right\} \qquad (98)$$

From these equations it follows that the critical volume, pressure, and temperature are all completely determined by the constants of equation (90).

Using the values of a, b, and R in equation (94), and substituting in (98), we have for carbon dioxide:

$$p_c = 61 \cdot 2 \text{ atmospheres},$$
$$T_c = 305 \cdot 3^\circ \text{ Absolute, or } 32 \cdot 2^\circ \text{ C.}$$

The experimental values as determined by Andrews are 72 atmospheres and 30·9° C.

It is frequently assumed that the approximate agreement between the calculated and experimental values of the critical temperature for carbon dioxide is a sufficient verification of Van der Waals' theory, but the constant b cannot be calculated with the required degree of accuracy from Regnault's experiments to make this an adequate test of the theory.

Also from equations (98) we have:

$$\frac{RT_c}{p_c v_c} = \frac{8}{3} = 2 \cdot 67,$$

whereas experiment shows that about 3·7 is the average value of this ratio, varying considerably, however, from gas to gas.

52. The Reduced Equation.—If the pressure, volume, and temperature of the fluid are expressed as fractions of the critical pressure, volume, and temperature the reduced form of Van der Waals' equation is obtained. Thus, writing

$$p = ep_c = \frac{ea}{27b^2},$$
$$v = nv_c = 3nb,$$
$$T = mT_c = \frac{8}{27} \cdot \frac{ma}{bR},$$

and substituting these values in equation (90), this reduces to

$$\left(e + \frac{3}{n^2}\right)(3n - 1) = 8m.$$

In this "reduced" equation the three constants which characterised a particular fluid have disappeared. The equation is accordingly true of any substance which satisfies an equation of the Van der Waals type, and the form of the curves connecting e, n, and m is the same for all these substances. Thus we see that two substances, the behaviour of each of which is represented by Van der Waals' equation, will be in corresponding states when the pressure, volume, and temperature are the same multiples of their critical values.

This theorem of corresponding states, enunciated by Van der Waals, was tested by Amagat and found to be approximately true for a large number of fluids. S. Young* has also tested the theorem by experiments upon the halogen derivatives of benzene.

The theorem of corresponding states is not unique to the equation of Van der Waals. Any equation of state giving a critical point and having not more than three constants will serve equally well to give a reduced equation, in which the constants peculiar to any one fluid disappear, and therefore become the basis of the theorem of corresponding states.

It must be remembered in applying the theorem that the accuracy of results deduced by its aid cannot be greater than the accuracy with which the original equation represents the behaviour of the fluids under consideration.

53. Amagat's Experiments.—In Chapter I the experiments of Amagat upon the compression of gases were discussed and the general nature of the results indicated.

Van der Waals' equation accounts for the variation of the product pv with increasing pressure, in the manner obtained experimentally by Amagat.

Writing equation (90) in the form

$$pv = \frac{RTv}{v-b} - \frac{a}{v},$$

and differentiating with respect to p, keeping T constant, we have:

$$\left(\frac{d(pv)}{dp}\right)_T = \left\{\frac{a}{v^2} - \frac{RTb}{(v-b)^2}\right\}\left(\frac{dv}{dp}\right)_T \quad . \quad . \quad . \quad (99)$$

Since the condition for a minimum on any isothermal is

$$\left(\frac{d(pv)}{dp}\right)_T = 0,$$

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* S. Young, *Phil. Mag.*, **33**, 153 (1892).

the right-hand side of equation (99) must vanish at this point. Now $\left(\frac{dv}{dp}\right)_T$ is never zero, so we have as the condition for a minimum:

$$\frac{RTb}{(v-b)^2} = \frac{a}{v^2},$$

or

$$RT \cdot \frac{b}{a} = \left(1 - \frac{b}{v}\right)^2. \quad . \quad . \quad . \quad . \quad (100)$$

This equation shows that the volume at which the minimum value of pv occurs on any isothermal gradually increases as the temperature is raised.

To find the locus of minima the temperature T must be eliminated from equation (100) by substitution from the original equation. Thus from equation (90):

$$RT = \left(p + \frac{a}{v^2}\right)(v - b),$$

and substituting this in equation (100) we have:

$$\frac{b}{a}\left(p + \frac{a}{v^2}\right)(v - b) = \left(1 - \frac{b}{v}\right)^2,$$

which reduces to

$$v = b\left(\frac{pv^2}{a} + 2\right).$$

Multiply each side of this equation by p, and put $pv = y$ and $p = x$, and we obtain:

$$y = b\left(\frac{y^2}{a} + 2x\right),$$

or

$$y(a - by) = 2abx.$$

This expression gives the locus of minima and is a parabola with axis parallel to the x axis as shown in Fig. 22.

Consider the isothermal which goes through the point A. Here $x = 0$ and $y = \frac{a}{b}$.

Writing Van der Waals' equation in terms of x and y we have:

$$\left(1+\frac{ax}{y^2}\right)(y-bx)=RT,$$

and substituting the coordinates of the point A:

$$RT=\frac{a}{b},$$

or

$$T=\frac{a}{bR}. \quad \ldots \ldots \quad (101)$$

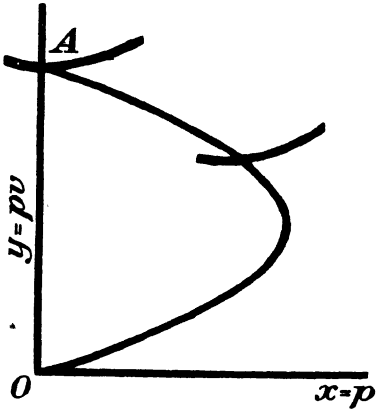

FIG. 22.

For temperatures above that given by equation (101) the minima lie in the region of negative pressure, so an Amagat isothermal for a temperature equal to or greater than $\frac{a}{bR}$ will slope upwards along its whole length for increasing values of p, but for a temperature less than $\frac{a}{bR}$ the isothermals first dip to a minimum and then rise.

Using the result from equation (98):

$$T_c=\frac{8}{27}\frac{a}{bR},$$

we see that the limiting temperature for an isothermal to show a minimum is:

$$T = \tfrac{27}{8} \cdot T_c.$$

The reason for Amagat finding no dip in the isothermals for hydrogen is now apparent. The critical temperature is 35° K, and therefore the limiting temperature above which minima do not occur is $\frac{27}{8} \times 35 = 118{\cdot}1$° K, or − 155° C., and all Amagat's experiments were conducted between 0° C. and 100° C.

54. The Cooling Effect.—It was stated in Chapter V that most gases show an inversion of the cooling effect at a certain temperature. The equation of Van der Waals indicates at what temperature this occurs.

We have

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT, \quad . \quad . \quad . \quad . \quad (90)$$

and differentiating with respect to T, keeping p constant:

$$\left\{p - \frac{a}{v^2} + \frac{2ab}{v^3}\right\}\left(\frac{dv}{dT}\right)_p = R,$$

or

$$\left(\frac{dv}{dT}\right)_p = \frac{R}{\left\{p - \frac{a}{v^2} + \frac{2ab}{v^3}\right\}}.$$

Substituting this value of $\left(\frac{dv}{dT}\right)_p$ in equation (60) for the cooling effect we have:

$$c_p\mu = \frac{RT}{\left\{p - \frac{a}{v^2} + \frac{2ab}{v^3}\right\}} - v,$$

and substituting for RT from equation (90) this reduces to:

$$c_p\mu = \frac{-bp + \frac{2a}{v} - \frac{3ab}{v^2}}{p - \frac{a}{v^2} + \frac{2ab}{v^3}}.$$

The denominator of this expression is always positive, since it is $R\left(\frac{dT}{dv}\right)_p$. Hence the cooling effect, μ, is positive if

$$bp < \frac{2a}{v} - \frac{3ab}{v^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (102)$$

and negative if

$$bp > \frac{2a}{v} - \frac{3ab}{v^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (103)$$

and inversion occurs when

$$bp = \frac{2a}{v} - \frac{3ab}{v^2},$$

or

$$p = \frac{a}{b}\left(\frac{2}{v} - \frac{3b}{v^2}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad (104)$$

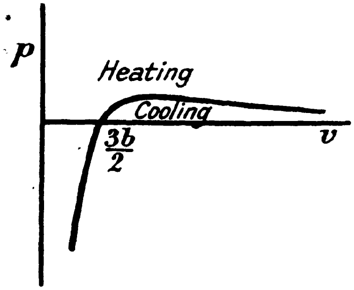

FIG. 23.

To obtain the temperature of inversion this equation must be combined with the original equation. Thus

$$\frac{2a}{b}\left(1 - \frac{b}{v}\right)^2 = RT. \quad . \quad . \quad . \quad . \quad . \quad . \quad (105)$$

As v is necessarily always greater than b, it will be seen that as v increases so also does the temperature of inversion.

The form of curve given by equation (104) is shown in Fig. 23. The pressure is zero when $v = \frac{3b}{2}$, or infinity. These values of v determine the limiting values of the temperature of inversion, as it is only between these limits that p is positive. Substituting these limits of v in equation (105) the limiting values of the temperature of inversion are $\frac{2}{9}\frac{a}{bR}$ and $\frac{2a}{bR}$, or from (98), $\frac{3}{4}T_c$ and $\frac{27}{4}\cdot T_c$.

As equation (104) is a quadratic there are two values of v for a constant value of p at which inversion occurs, as may also be seen by reference to Fig. 23. Consequently by equation (105) there are two temperatures for a constant value of p at which inversion occurs. As the temperature increases through the lower of these values the change is from a heating to a cooling effect, and as it increases through the higher of these values the change is from a cooling to a heating effect.

The maximum value of p for inversion to occur is $\frac{a}{3b^2}$, when $v = 3b$. For any value of p less than this there is a cooling effect provided the condition of the substance is represented by a point inside the area enclosed by the curve and the axis of volume, Fig. 23, and for any greater value of p there is a heating effect as indicated by equations (102) and (103) respectively.

Consider the case of hydrogen. In the experiments of Joule and Thomson the pressure used was 4·7 atmospheres. The critical temperature and pressure are 35° K and 15 atmospheres. From equation (104) we can find the values of $\frac{b}{v}$ corresponding to the pressure used by Joule and Thomson, and by substitution in equation (105) find the two temperatures at which inversion occurs at this pressure. Equation (104) can be written:

$$p = 27p_c\left[2\frac{b}{v} - 3\left(\frac{b}{v}\right)^2\right].$$

Hence

$$\frac{b}{v} = \frac{2 \pm \sqrt{4 - \frac{12\,p}{27\,p_c}}}{6},$$

$$= 0{\cdot}6608 \text{ or } 0{\cdot}0058,$$

by substitution of the above values for p and p_c.

Writing equation (105) in the form

$$T = \frac{27}{4} T_c \left(1 - \frac{b}{v}\right)^2,$$

we have by substitution for $\frac{b}{v}$:

$$T = 233{\cdot}5^\circ \text{ or } 27{\cdot}2^\circ,$$

that is, below $-245{\cdot}9^\circ$ C. there would be a heating effect, between $-245{\cdot}9^\circ$ C. and $-39{\cdot}6^\circ$ C. a cooling effect, and above $-39{\cdot}6^\circ$ C. a heating effect. Thus Van der Waals' equation qualitatively accounts for the heating effect observed at ordinary temperatures.

55. The Specific Heat Equations.—From equation (54) we have:

$$\left(\frac{dc_p}{dp}\right)_T = -T\left(\frac{d^2v}{dT^2}\right)_p.$$

Differentiating Van der Waals' equation with respect to T at constant p, we obtain:

$$\left(\frac{d^2v}{dT^2}\right)_p = -\frac{R^2 . \frac{2a}{v^3}\left(1 - \frac{3b}{v}\right)}{\left(p - \frac{a}{v^2} + \frac{2ab}{v^3}\right)^3}.$$

Hence $\left(\frac{dc_p}{dp}\right)_T$ is positive, negative, or zero according as v is greater, less than, or equal to $3b$, a result in general agreement with experiment.

Similarly from equation (51):

$$\left(\frac{dc_v}{dv}\right)_T = T\left(\frac{d^2p}{dT^2}\right)_v,$$

and Van der Waals' equation gives $\left(\frac{d^2p}{dT^2}\right)_v = 0.$

Hence c_v should be independent of the density. It is found by experiment, for instance in Joly's* work, that the specific heat at constant volume of air and carbon dioxide increases with increasing density, whilst that of hydrogen diminishes.

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* Joly, *Proc. Roy. Soc.*, **47**, 218 (1889).

56. Callendar's Equation.—Callendar's equation (67) may be written:

$$v = \frac{RT}{p} - c + b.$$

The quantity b is the co-volume and represents the actual volume occupied by the molecules. As a first approximation it can be taken as the volume occupied by the substance when all condensed to a liquid. The quantity c is the co-aggregation volume, and expresses the diminution of volume produced by the formation of molecular clusters; this varies inversely as T^n, n having different values for different gases and vapours.

It must be remembered that the equation makes no attempt to represent the phenomena of the critical state, but only to represent accurately the experimental results for a vapour, whether saturated or superheated, when the pressure is considerably below the critical pressure.

57. Amagat's Experiments.—Writing the equation in the form

$$pv = RT - cp + bp,$$

and differentiating with respect to p:

$$\left(\frac{d(pv)}{dp}\right)_T = -c + b. \quad . \quad . \quad . \quad . \quad (106)$$

Hence the Amagat isothermals are straight lines which incline away or towards the pressure axis depending upon whether b is greater than or less than c. The quantity c is dependent upon the temperature, becoming smaller as the temperature rises, and therefore if the isothermal for a certain temperature is inclined towards the pressure axis, as the temperature rises the slope becomes less, the isothermal being parallel to the pressure axis at $c = b$, and for higher temperatures inclining away from this axis for increasing pressure. There is nothing in equation (106) to account for a change of slope, and in this respect the equation fails.

58. The Specific Heat Equations.—Writing the equation in the form:

$$v = \frac{RT}{p} - c + b,$$

and remembering that c can be expressed:

$$c = c_1\left(\frac{T_1}{T}\right)^n,$$

where c_1 is the value at the temperature T_1, we have by differentiation of (67):

$$\left(\frac{d^2v}{dT^2}\right)_p = -\frac{n(n+1)c}{T^2}.$$

Therefore using equation (54):

$$\left(\frac{dc_p}{dp}\right)_T = \frac{n(n+1)c}{T}.$$

This equation on integration becomes:

$$c_p = (c_p)_0 + \frac{n(n+1)cp}{T}, \quad . \quad . \quad . \quad (107)$$

where $(c_p)_0$ is the limiting value of c_p as p approaches zero at the temperature T. Callendar assumes that the limiting value $(c_p)_0$ is the same for all temperatures at which the equation applies, for when $p = 0$ the gas is infinitely rarefied and will behave as a perfect gas, of which the specific heat is constant.

For the specific heat at constant volume it is convenient to write the equation in the form:

$$pU = RT, \quad . \quad . \quad . \quad . \quad . \quad . \quad (108)$$

where

$$U = v - b + c, \quad . \quad . \quad . \quad . \quad . \quad . \quad (109)$$

and this is a function of v and T only.

Differentiating equation (108) with respect to T we have:

$$U\left(\frac{dp}{dT}\right)_v + p\left(\frac{dU}{dT}\right)_v = R, \quad . \quad . \quad . \quad (110)$$

and differentiating again:

$$U\left(\frac{d^2p}{dT^2}\right)_v + 2\left(\frac{dU}{dT}\right)_v \cdot \left(\frac{dp}{dT}\right)_v + p \cdot \left(\frac{d^2U}{dT^2}\right)_v = 0. \quad (111)$$

Also differentiating equation (109):

$$\left(\frac{dU}{dT}\right)_v = -\frac{nc}{T}, \quad \left(\frac{d^2U}{dT^2}\right)_v = \frac{n(n+1)c}{T^2}.$$

Substituting in equation (110) for $\left(\frac{dU}{dT}\right)_v$ and $\frac{R}{U}$ from equation (108), we have:

$$\left(\frac{dp}{dT}\right)_v = \frac{p}{T}\left(1 + \frac{nc}{U}\right).$$

This substituted in equation (111) gives:

$$\left(\frac{d^2p}{dT^2}\right)_v = \frac{Rnc}{TU^2}\left(1 - n + \frac{2nc}{U}\right).$$

Hence from equation (51):

$$\left(\frac{dc_v}{dv}\right)_T = \frac{Rnc}{U^2}\left(1 - n + \frac{2nc}{U}\right).$$

At constant temperature $dU = dv$, so on integration this becomes:

$$\begin{aligned} c_v &= \frac{Rnc}{U}\left(n - 1 - \frac{nc}{U}\right) + (c_v)_0, \\ &= \frac{p}{T}nc\left(n - 1 - \frac{pnc}{RT}\right) + (c_v)_0, \quad . \quad . \quad . \quad (112) \end{aligned}$$

where $(c_v)_0$ is the limiting value of c_v as p approaches zero, and is considered as having the same value for all values of T.

For the difference of specific heats we have by equation (55):

$$c_p - c_v = T\left(\frac{dp}{dT}\right)_v \cdot \left(\frac{dv}{dT}\right)_p,$$

which on substitution of the values already obtained for the differential coefficients reduces to:

$$c_p - c_v = R\left(1 + \frac{nc}{U}\right)^2. \quad . \quad . \quad . \quad . \quad (113)$$

In the limit as p approaches zero, U becomes infinitely great and $\frac{nc}{U}$ vanishingly small. Hence in the limit:

$$(c_p)_0 - (c_v)_0 = R, \quad . \quad . \quad . \quad . \quad . \quad (114)$$

a similar result to that obtained for a perfect gas, in this case, however, holding only when the pressure is vanishingly small.

59. The Cooling Effect.—Substituting for $\left(\frac{dv}{dT}\right)_p$ from Callendar's equation in equation (60), we have:

$$\begin{aligned} c_p\mu &= T\left(\frac{R}{p} + \frac{nc}{T}\right) - v, \\ &= v + c - b + nc - v, \\ &= (n+1)c - b. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (115) \end{aligned}$$

Thus the cooling effect is positive if $(n + 1)c$ is greater than b and negative if $(n + 1)c$ is less than b, inversion occurring when these two terms are equal. The temperature of inversion is therefore given by:

$$(n+1)c_1\left(\frac{T_1}{T}\right)^n = b.$$

This may be expressed in a slightly different form. From equation (115) inversion occurs when

$$nc = -c + b,$$

or from equation (106) when

$$nc = \left(\frac{d(pv)}{dp}\right)_T, \quad . \quad . \quad . \quad . \quad . \quad . \quad (116)$$

or if the Amagat isothermal slopes upwards with a gradient greater than nc there is a heating effect, and for a gradient less than nc a cooling effect.

The method of calculation of the co-aggregation volume is to use equation (115). Substituting in this the value of c_p given by equation (107) we have:

$$\mu\left((c_p)_0 + \frac{n(n+1)cp}{T}\right) = (n+1)c - b,$$

or

$$c = \frac{\mu(c_p)_0 + b}{(n + 1)\left\{1 - \frac{\mu n p}{T}\right\}}.$$

All the quantities on the right-hand side of this equation are known, and hence by a series of determinations of the cooling effect μ at different temperatures the variation of c can be found.

Another way of finding c is to use equation (116), but owing to the difficulty of measuring the slope of an Amagat isothermal accurately, the results so obtained would possibly have a large error, besides giving the value of c for only one temperature, i.e. that of inversion.

60. Calculation of Entropy, Internal Energy, and Total Heat.

(i) *Entropy.*—The change of entropy in any process can be written:

$$dS = \left(\frac{dS}{dT}\right)_p dT + \left(\frac{dS}{dp}\right)_T dp,$$

$$= \frac{c_p}{T}dT - \left(\frac{dv}{dT}\right)_p dp.$$

Substituting for c_p from equation (107) and for $\left(\frac{dv}{dT}\right)_p$ from Callendar's equation, this becomes:

$$dS = \frac{(c_p)_0}{T}dT + \frac{n(n+1)cp}{T^2}dT - \frac{R}{p}dp - \frac{nc}{T}dp,$$

$$= \frac{(c_p)_0}{T}dT - \frac{R}{p}dp - n \,.\, d\left(\frac{cp}{T}\right) \quad . \quad . \quad . \quad . \quad (117)$$

Integrating we have:

$$S = (c_p)_0 \log T - R \log p - \frac{ncp}{T} + C, \quad . \quad . \quad (118)$$

where C is a constant of integration.

It is interesting to compare this expression for the entropy of a substance which deviates considerably from a perfect gas with equation (37) for that of a perfect gas. It will be seen to be the same except for the addition of a small term depending upon the co-aggregation volume c. The magnitude of this term is a measure of the imperfectness of the vapour.

(ii) *Internal Energy.*—The expression for the change of internal energy in a process is:

$$dE = TdS - pdv.$$

Substituting for dS from equation (117) and for dv from Callendar's equation:

$$dE = [(c_p)_0 - R]\,dT + n\left(\frac{ncp}{T}dT - cdp\right),$$

which by use of equation (114) reduces to:

$$dE = (c_v)_0\,dT - n\,.\,d(cp).$$

Integrating we have:

$$E = (c_v)_0T - ncp + B. \quad . \quad . \quad . \quad . \quad (119)$$

(iii) *Total Heat.*—The total heat H is defined by the equation:

$$H = E + pv.$$

Substituting for E from equation (119) and for pv from Callendar's equation, we have:

$$\begin{aligned} H &= (c_v)_0T - ncp + B + RT - cp + bp, \\ &= (c_p)_0 T - \{(n + 1)c - b\}p + B, \end{aligned}$$

which by equation (115) becomes:

$$H = (c_p)_0T - c_p\mu p + B. \quad . \quad . \quad . \quad (120)$$

Hence if H be plotted against p the isothermals are straight lines.

61. Application to Steam.—From experiments upon dry steam it was found by Callendar that the adiabatic relation between pressure and temperature could be expressed by the simple law:

$$\frac{p}{T^{n+1}} = \text{constant}.$$

This law was tested over a wide range of conditions, and the value of n was found to be $\frac{10}{3}$, and independent of both the pressure and temperature. A mathematical investigation of the problem revealed the fact that this surprising result for a vapour which departs widely from the perfect gas laws could be explained if the internal energy could be written:

$$E = np(v - b) + B. \quad . \quad . \quad . \quad . \quad (121)$$

It follows that the total heat, H, is of the form:

$$H = (n + 1)p(v - b) + bp + B.$$

As the specific heats at constant volume and constant pressure are the rates of variation of E and H with temperature, we have:

$$c_v = n(v - b)\left(\frac{dp}{dT}\right)_v,$$

$$c_p = (n + 1)p\left(\frac{dv}{dT}\right)_p.$$

Substituting these values in equation (55) we have:

$$T = (n + 1)p \,.\left(\frac{dT}{dp}\right)_v - n(v - b)\left(\frac{dT}{dv}\right)_p,$$

a differential equation for T, the general solution of which is:

$$\frac{p(v - b)}{T} = F\left(\frac{p}{T^{n+1}}\right), \quad . \quad . \quad . \quad . \quad (122)$$

where F is an arbitrary function of $\frac{p}{T^{n+1}}$, which remains constant in adiabatic change.

Callendar's equation is a special case of the more general equation (122), obtained by replacing the function F by $R + \frac{kp}{T^{n+1}}$, R being the constant to which $\frac{p(v - b)}{T}$ approximates when p is very small, and k a constant.

Consequently the relations which have been deduced from Callendar's equation apply in the case of steam, and by virtue of the extremely simple relation for E many of them reduce to simpler forms.

Consider first the internal energy. Using Callendar's equation (67), equation (121) can be written:

$$E = n(RT - cp) + B,$$

and comparing this with equation (119):

$$(c_v)_0 = nR. \quad . \quad . \quad . \quad . \quad . \quad . \quad (123)$$

Hence as

$$(c_p)_0 - (c_v)_0 = R,$$

$$(c_p)_0 = (n + 1)R. \quad . \quad . \quad . \quad . \quad . \quad (124)$$

Substituting these values for $(c_v)_0$ and $(c_p)_0$ in equations (107), (112), (119), (120), and (118), we obtain the following equations for steam:

$$c_p = (n + 1)\left\{R + \frac{ncp}{T}\right\}.$$

$$c_v = nR + \frac{ncp}{T}\left(n - 1 - \frac{ncp}{RT}\right).$$

$$E = nRT - ncp + B.$$

$$H = (n + 1)\{RT - cp\} + bp + B. \quad . \quad . \quad . \quad (125)$$

$$S = (n + 1)R \log T - R \log p - \frac{ncp}{T} + B. \quad (126)$$

This last equation for the entropy can be written:

$$S = R \log \frac{T^{n+1}}{p} - nk\frac{p}{T^{n+1}} + B,$$

where c is replaced by $\frac{k}{T^n}$. Now we have already seen that in an adiabatic change the entropy is constant, and hence $\frac{T^{n+1}}{p}$ is constant, which is the result found for steam by Callendar. The adiabatic relation may, by use of the original equation, be expressed in the equivalent forms:

$$(v - b)T^n = \text{constant},$$

$$\frac{p(v - b)}{T} = \text{constant},$$

$$p^n(v - b)^{n+1} = \text{constant}.$$

These relations are often more convenient than the expression for S when the initial state of the steam is given in terms of two of the variables, and it is required to find the final state in terms of the same pair of variables.

62. Equation of Saturation Pressure.—Suppose the entropy of saturated steam at a temperature T_1 and under a pressure p_1 is S_1. Then equation (126) can be expressed:

$$S - S_1 = (n + 1)R \log \frac{T}{T_1} - R \log \frac{p}{p_1} - \frac{ncp}{T} + \frac{nc_1p_1}{T_1}. \quad (127)$$

In effect this equation is the same as before, but the constant B has been expressed in terms of S_1, T_1, p_1, and c_1.

Now the entropy of steam at a temperature T is equal to the entropy of water at the same temperature, together with the quantity $\frac{l}{T}$, where l is the latent heat of vaporization at T. Denoting the entropy of water by S':

$$S = S' + \frac{l}{T},$$

and substituting this expression for S in equation (127) we have:

$$S' - S'_1 + \frac{l}{T} - \frac{l_1}{T_1} = (n + 1)R \log \frac{T}{T_1} - R \log \frac{p}{p_1} - \frac{ncp}{T} + \frac{nc_1p_1}{T_1} \quad (128)$$

This equation, obtained by equating the two expressions for the entropy of saturated steam, gives the relation between the saturation pressure p and the absolute temperature T. To use the equation in this form for the calculation of p would be inconvenient in practice, as S' and l involve p implicitly. It may be simplified, however, in the following manner.

It has been shown by Callendar that water is in equilibrium with its own vapour when the water has its own volume of vapour dissolved in it. Let us denote the volume of unit mass of steam by V and of unit mass of water by v. Then for water to be in equilibrium with its own vapour it contains a volume v of saturated steam. To vaporize the whole mass of liquid would require an amount of heat l, and the volume then occupied would be V, so the heat required to produce the vapour originally present in the water is $\frac{vl}{V-v}$. This heat has to be supplied whilst the water is being heated to the temperature of saturation, and therefore comprises part of the total heat of water. The other and chief part of the total heat can be considered as increasing linearly with the temperature. In steam tables the total heat of water at 0° C. and under its own saturation pressure is taken as zero, so denoting the total heat of water by h we have:

$$h = \sigma(T - T_0) + \frac{lv}{V - v} - \frac{l_0 v_0}{V_0 - v_0}, \quad . \quad . \quad . \quad (129)$$

where the suffixed letters, such as T_0, etc., denote the conditions at 0° C., and σ is a constant approximately equal to unity. This equation represents the experimental results with great accuracy.

To find the entropy of water at a temperature T, imagine it to be heated from 0° C. to the required temperature without the formation of any dissolved steam, and the steam all to be formed at the higher temperature. Then

$$\begin{aligned} S' &= \int_{T_0}^{T} \sigma \, . \, \frac{dT}{T} + \frac{lv}{T(V - v)} - \frac{l_0 v_0}{T_0(V_0 - v_0)}, \\ &= \sigma \log \frac{T}{T_0} + \frac{lv}{T(V - v)} - \frac{l_0 v_0}{T_0(V_0 - v_0)}. \quad . \quad (130) \end{aligned}$$

Now the latent heat of vaporization is the difference between the total heat of steam and that of water. Hence

$$l = H - h,$$

or

$$l = (n + 1)\{RT - cp\} + bp + B - \sigma(T - T_0) - \frac{lv}{V - v} + \frac{l_0 v_0}{V_0 - v_0}$$

by substitution for H and h from equations (125) and (129) respectively. This reduces to

$$\frac{lv}{V-v} = (n + 1)\{RT - cp\} + bp + B - \sigma(T - T_0) + \frac{l_0 v_0}{V_0 - v_0}. \quad (131)$$

Substituting for S' and S_1' in equation (128) from equation (130), and for l in the resulting equation from (131), we have as the equation of saturation pressure:

$$R \log \frac{p}{p_1} = l'\left(\frac{1}{T_1} - \frac{1}{T}\right)$$
$$+ \{(n+1)R - \sigma\}\left\{\log \frac{T}{T_1} - \left(1 - \frac{T_1}{T}\right)\right\} + \left[(c-b)\frac{p}{T}\right]_{T_1}^{T}, \quad (132)$$

where the last term has to be evaluated between the limits T_1 and T, and the value of l' is given by:

$$l' = \frac{V_1}{V_1 - v_1} l_1 + (n+1)c_1 p_1 - b p_1.$$

To calculate the saturation pressure at any temperature from equation (132) an approximate value of p is substituted on the right-hand side; the value of p then found will be near the correct value, and by the method of successive approximations the value can be found to any required degree of accuracy.

Table V, page 112, from Callendar's *Properties of Steam* shows how accurate is the agreement between equation (132) and the experimental results. This agreement is all the more remarkable when it is remembered that equation (132) contains not a single adjustable constant.

63. Other Equations of State.—There have been a large number of attempts to formulate an equation of state which will agree better with the experimental results than that of Van der Waals. Many of these are but modifications of this equation, whilst others have been formed to give exact quantitative results for certain phenomena.

Clausius proposed the equation:

$$\left(p + \frac{a'}{T(v+c)^2}\right)(v - b) = RT,$$

a', b, and c being constants. This equation has been modified by Berthelot and becomes:

$$\left(p + \frac{a'}{Tv^2}\right)(v - b) = RT,$$

which agrees better than Van der Waals' equation with the experimental results at moderate pressures, but fails just as badly at the critical point.

Dieterici gives the equation:

$$p = \frac{RT}{v - b} e^{-a/RTv},$$

a and *b* being constants and *e* the base of natural logarithms. This equation fails at high pressures.

TABLE V.

Temperature ° C.	Equation (132).	Knoblauch, Linde and Klebe.	Holborn and Henning.
0°	4·62	—	(4·58)
20°	17·59	—	(17·51)
40°	55·38	—	(55·31)
60°	149·38	—	149·19
80°	355·1	—	355·1
110°	1,075·0	1,074·3	1,074·5
120°	1,490·5	1,489	1,488·9
130°	2,028·8	2,025	2,025·6
140°	2,715·3	2,710	2,709·5
150°	3,577·7	3,567	3,568·7
160°	4,646	4,634	4,633
170°	5,953	5,939	5,937
180°	7,532	7,514	7,514
190°	9,420	—	9,404
200°	11,653	—	11,647

Pressures in millimetres of mercury. The third and fourth columns give the experimental results. Those in brackets were obtained by Theisen and Scheel, and are included in the table given by Holborn and Henning.

Lees starts with the equation in the form:

$$\{p + \phi(p, v, T)\}(v - b) = RT,$$

and chooses the form of the function ϕ so that the equation fits certain experimental results. The final form at which he arrives is:

$$\left\{p + \frac{ap^{1/3}}{Tv^{5/3}}\right\}(v - b) = RT.$$

It is left to the student to test how these equations fit the general experimental results.

CHAPTER VII

THERMODYNAMICS OF CHANGE OF PHASE

64. Clapeyron's Equation.—When a substance changes phase, as, for instance, in the fusion of a solid, or the vaporization of a liquid, there are volume changes accompanying the thermal effects. In any change of phase the work done in the expansion against the external pressure, together with the change in internal energy of the substance, is equal to the heat supplied to effect the transformation, namely l, the latent heat.

The connection between the latent heat and the other physical properties of a substance can be obtained by a variety of methods, of which the following is, perhaps, the simplest. From equations (47) we have:

$$\left(\frac{dS}{dv}\right)_T = \left(\frac{dp}{dT}\right)_v, \quad . \quad . \quad . \quad . \quad . \quad (133)$$

the second thermodynamic relation. In a change of phase, the heat communicated to the substance is the latent heat l. Suppose the process takes place at the absolute temperature T, which is constant for the whole transformation, then the change of entropy is $\frac{l}{T}$. The change of volume is the difference between the specific volumes in the final and initial phases; denoting these by v_2 and v_1 respectively we have:

$$\text{Change of volume} = dv = v_2 - v_1.$$

Substituting these expressions for the change of entropy and change of volume in equation (133), this becomes:

$$\frac{l}{T} = (v_2 - v_1)\left(\frac{dp}{dT}\right)_v. \quad . \quad . \quad . \quad . \quad . \quad (134)$$

This equation was first obtained by Clapeyron,* after whom it is named, in 1834. In applying the equation to vaporization, $\frac{dp}{dT}$ must be taken as the rate of variation of the saturation pressure with temperature, which is the same as $\left(\frac{dp}{dT}\right)_v$ if both liquid and vapour are present.

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* Clapeyron, *Journ. École Polyt.*, **14**, 153 (1834).

65. Equations of Clapeyron and Clausius.—A more instructive method of deducing the Clapeyron equation is by the use of a $p - v$ diagram. In Fig. 24 AB and CD represent the portions of isothermals, at temperatures T and $T + dT$ respectively, where the substance is changing from the liquid to the gaseous phase. The parabolic curve is the boundary curve, along the portion AD the substance being in the liquid phase, and along CB in the vapour phase. Any point inside this boundary curve represents the liquid in the presence of its vapour.

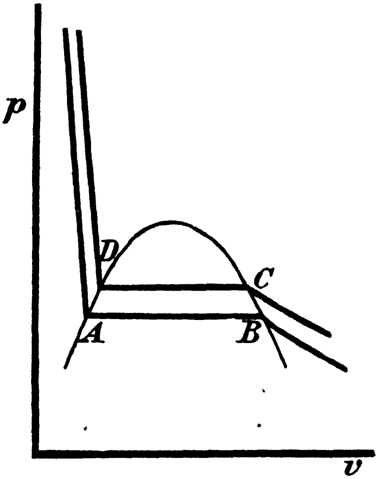

FIG. 24.

Let unit mass of substance be taken round the closed curve DCBAD. Suppose the latent heat of vaporization at a temperature T is l, and at $T + dT$ is $l + dl$, then these amounts of heat will be rejected and absorbed respectively in describing the cycle. These will not be the only heat transferences in the cycle, because the temperature changes progressively in moving from A to D and from C to B. In these parts of the cycle amounts of heat $s_1 dT$ and $s_2 dT$ will be absorbed and rejected, where s_1 and s_2 are the specific heats of the substance when conditions are so adjusted that it is constrained to move along the boundary curves AD and CB. Hence the net amount of heat absorbed in describing the cycle is:

$$l + dl - s_2 dT - l + s_1 dT,$$

repeated with certain modifications by Dewar,* who obtained the mean value 0·00720° C.

67. The Specific Heat of a Saturated Vapour.—In deducing equation (137) it was pointed out that s_1 and s_2 are the specific heats of the substance when it is constrained to move along the liquid and vapour boundary curves respectively. These specific heats are different in value from either the specific heat at constant pressure or at constant volume, although in the case of a solid or liquid c_p may be substituted for s_1 or s_2 without serious error. When considering the change from liquid to vapour, however, s_2 is the heat required to raise the temperature of unit mass of the vapour one degree, when the pressure is so varied as to keep the vapour saturated throughout the process: that is, s_2 in this case is the specific heat of the saturated vapour. This may be either positive, negative, or zero.

Using equation (137), we can calculate the specific heats of saturated vapours. As an example of a negative specific heat consider the case of saturated steam at 100° C. Here we have:

T = absolute temperature of steam point = 373·1°.
s_1 = specific heat of water at 100° C. = 1·007.
l = latent heat of water at 100° C. = 539·30.
$\frac{dl}{dT}$ = variation of latent heat of water with temperature at 100° C. = − 0·604.

(This last value is obtained from *The Callendar Steam Tables*, and gives the mean variation over the range 90° C. to 110° C.)

Writing equation (137) in the form:

$$s_2 - s_1 = \frac{dl}{dT} - \frac{l}{T},$$

and substituting the above values we have:

$$\begin{aligned} s_2 &= 1\cdot007 - 0\cdot604 - \frac{539\cdot3}{373\cdot1}, \\ &= -1\cdot042. \end{aligned}$$

The negative sign means that this amount of heat has to be removed in order to raise the temperature of unit mass of saturated steam one degree Centigrade. This seemingly paradoxical result is easily understandable when it is remembered that work has to be done on the vapour in order to keep it saturated, and this work may be more than sufficient to raise its temperature by the required amount, in which case heat will have to be removed or the temperature will rise still further. This result for steam was predicted independently by Rankine and Clausius in 1850.

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* Dewar, *Proc. Roy. Soc.*, **30**, 553 (1880).

68. Temperature-Entropy Diagrams for Saturated Vapours.—The specific heat of a saturated vapour may most conveniently be studied by means of temperature-entropy diagrams.* To draw such a diagram it is first necessary to calculate the entropy of the liquid under its saturation pressure at a temperature T, suppose this to be S_1, and then to add $\frac{l}{T}$ to find the entropy of the saturated vapour, say S_2. Expressed mathematically:

$$S_2 = S_1 + \frac{l}{T}.$$

Differentiation of this equation yields the Clausius equation. If the entropy of a liquid is arbitrarily assigned the value zero at 0° C., the entropy at a temperature t° C. is:

$$S_1 = \int^t \frac{c_p}{T} dT,$$

where c_p is the specific heat of the liquid at constant pressure, namely, the saturation pressure for the given temperature, and the liquid is supposed to be subjected to this pressure for the whole of the heating process. Consequently when an empirical formula connecting c_p with temperature is available, S_1 and S_2 may be readily calculated. In Figs. 25 and 26 the temperature-entropy curves for water† and ether, and benzene and acetic acid have been drawn from the data given by Ewing (*loc. cit.*).

Consider a small step along the saturated vapour boundary curve. The heat taken in is s_2dT, by the definition of s_2, and this is equal to TdS_2. Hence

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* Ewing, *Phil. Mag.*, **39**, 633 (1920).

† This curve is drawn from data in Callendar's *Properties of Steam*.

$$s_2dT = TdS_2,$$

or

$$s_2 = T\frac{dS_2}{dT}.$$

The specific heat of a saturated vapour will therefore be negative for all conditions which make its entropy decrease with rise in temperature, or the specific heat is positive only when the slope of the saturation line on the temperature-entropy diagram is positive. From Figs. 25 and 26 it will be seen that the specific heat of saturated steam is always negative, whereas for ether, benzene, and acetic acid it is positive, zero, and negative, depending upon the temperature. In the neighbourhood of the critical point the specific heat of any saturated vapour necessarily becomes negative, for here the saturated vapour boundary curve bends round to meet the liquid boundary curve.

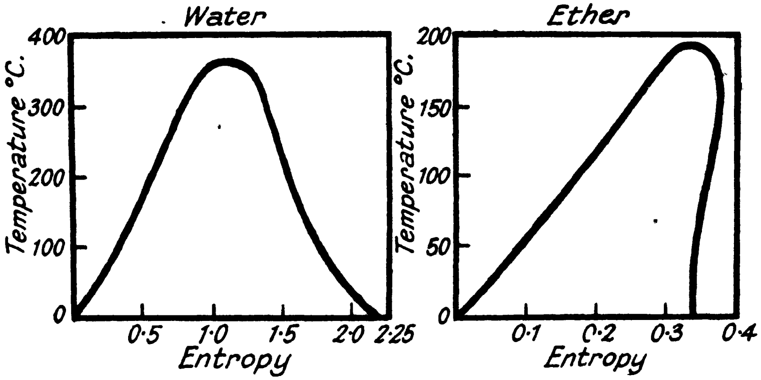

FIG. 25.

Temperature-Entropy Curves for Water and Ether.

Let us now consider what happens if a saturated vapour is allowed to expand adiabatically. In such an expansion the entropy remains constant and the temperature falls. From the temperature-entropy diagrams it will be seen that if the specific heat s_2 is negative the expansion causes supersaturation or partial condensation, but if the specific heat is positive the vapour will become superheated, the reverse effects occurring for adiabatic compression.

Experiments were made by Hirn* to verify these results. Saturated steam at a pressure of 5 atmospheres was enclosed in a long cylinder, the ends of which were closed by parallel glass plates. On suddenly opening a tap so that the steam was free to expand, a dense cloud formed within the cylinder, showing that part of the vapour had condensed. Repeating the experiment with ether vapour instead of steam, no such condensation was observed on expansion, but on adiabatic compression condensation occurred, showing that the specific heat of saturated ether vapour under the conditions of the experiment was positive. Cazin† repeated these experiments with an improved apparatus, and determined the temperatures at which inversion from positive to negative values of the specific heat of the saturated vapour occurred for various substances.

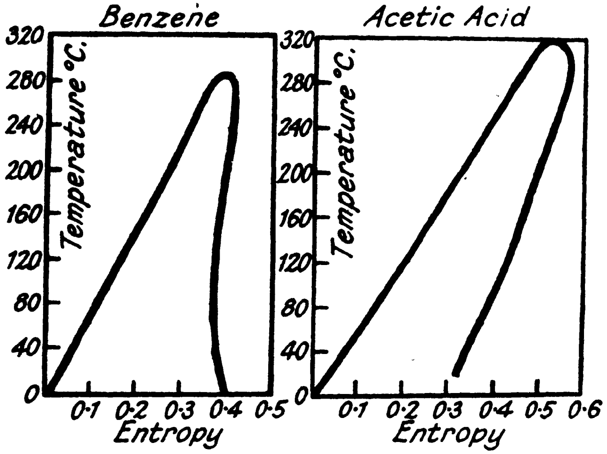

FIG. 26.

Temperature-Entropy Curves for Benzene and Acetic Acid.

69. Alternative Equations for the Specific Heat of a

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* Hirn, *Cosmos*, **22**, 413 (1863).

† Cazin, *Ann. de Chim. et de Phys.*, **14**, 374 (1868).

Saturated Vapour.—In considering the variation of the specific heat at constant volume (Section 40) we deduced the equation:

$$\delta q = c_v dT + T\left(\frac{dp}{dT}\right)_v dv.$$

Hence the specific heat of a saturated vapour is given by

$$s_2 = \left(\frac{\delta q}{dT}\right)_s = c_v + T\left(\frac{dp}{dT}\right)_v\left(\frac{dv}{dT}\right)_s,$$

where the suffix s is used to denote the conditions along the saturation line. The quantity $\left(\frac{dv}{dT}\right)_s$ is the rate of change of the saturation volume with temperature, and for the majority of substances this is a negative quantity; hence s_2 may be positive or negative, depending upon the relative magnitudes of the terms upon the right-hand side. By the use of Clapeyron's equation this equation may be written in the form:

$$s_2 = c_v + \frac{l}{v_2 - v_1}\left(\frac{dv}{dT}\right)_s.$$

Similarly commencing with the equation:

$$\delta q = c_p dT - T\left(\frac{dv}{dT}\right)_p dp,$$

we obtain:

$$s_2 = c_p - T\left(\frac{dv}{dT}\right)_p \cdot \left(\frac{dp}{dT}\right)_s,$$

or

$$s_2 = c_p - \frac{l}{(v_2 - v_1)}\left(\frac{dv}{dT}\right)_p.$$

In this equation the value of $\left(\frac{dv}{dT}\right)_p$ has to be calculated for the unsaturated vapour, and the saturation values of p, v, and T afterwards substituted.

70. The Triple Point.—The relation between the equilibrium pressure and the temperature of a mixture of a liquid in contact with its own vapour can be represented by a line such as PA, Fig. 27. This curve gives the saturation pressure of a liquid at any temperature. Similarly, if a solid is in contact with the liquid form of the same substance, the relation between the equilibrium pressure and temperature can be represented by a line such as PB. A third line, PC, represents the connection between pressure and temperature for the solid in contact with the vapour. It is only when the conditions of temperature and pressure correspond to some point on one of these three lines that any two of the modifications of a substance are able to exist together in equilibrium. Suppose we have a mixture of liquid and vapour whose conditions are represented by some point on the line PA. If the temperature of the mixture is raised, the pressure remaining constant, the conditions will no longer be represented by a point on PA, but by some point in the area bounded by PA and PC. These areas, bounded by the three curves, correspond to the existence of but a single modification. Thus for a mixture the pressure and temperature cannot be independently varied if a mixture in equilibrium is to be retained. For a single modification, however, the pressure and temperature can both be varied, within the limits imposed by the curves, without disturbing the equilibrium. We shall return to this subject in the next chapter.

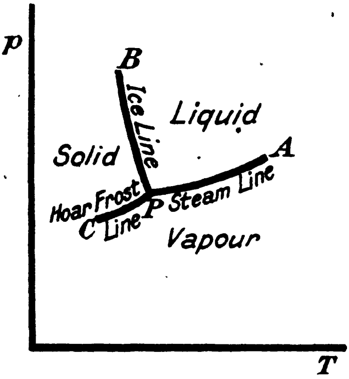

FIG. 27.
Triple Point for Water.

In the case of water the three lines, PA, PB, PC, are known as the steam, ice, and hoar-frost lines respectively. From the early researches of Regnault it was considered that the hoar-frost line was simply a continuation of the steam line, but Kirchhoff subsequently showed that these two lines are distinct and intersect at an angle. It was later discovered by James Thomson that the steam, ice, and hoar-frost lines intersect at a common point. Obviously this point corresponds to the co-existence in equilibrium of the three modifications. Such a point is called a triple point.

The existence of a triple point can be demonstrated thermodynamically in the following manner. Consider a mixture of ice and water in equilibrium at the point where the ice line intersects the steam line. In order to demonstrate the existence of a triple point it will be sufficient to show that at the point under consideration the vapour pressure over the ice is the same as that over the water, for the temperature being the same for the ice, water, and vapour the three curves must intersect in a common point if the vapour pressures are also the same. Imagine an apparatus, such as that shown in Fig. 28, which contains ice and water in contact, and the vapours of these two states of the substance separated by a mechanism for the performance of external work. Now for any reversible cycle $\Sigma \frac{\delta q}{T}$ is zero, and hence for an isothermal reversible cycle $\Sigma\, \delta q$ is zero, or the heat absorbed and the external work done are both zero. We shall suppose the vapour over the ice to have a pressure p_1, whilst that over the water has a pressure p_2. Now perform the following cycle.

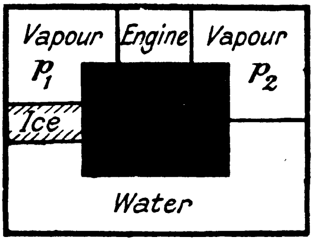

FIG. 28.

(i) Evaporate a mass dm of the ice into vapour at the pressure p_1. Heat of amount dml_{13} is absorbed and external work dmp_1v_1 performed, where l_{13} is the latent heat of transformation from ice to vapour and v_1 the specific volume of the vapour at the pressure p_1.

(ii) Allow this vapour to pass through the engine expanding isothermally and reversibly to the pressure p_2. External work of amount $dm\int_{v_1}^{v_2} pdv$ is done by the substance, and the same amount of heat absorbed, v_2 being the specific volume at the pressure p_2.

(iii) Condense the vapour to water, the heat given out being l_{23}, and work of amount dmp_2v_2 being done on the substance.

(iv) Allow the water so obtained to be frozen on to the ice. The heat given out in this process is l_{12}.

The system has now returned to its initial condition, and therefore by the application of the foregoing principle we have:

$$l_{13} + \int_{v_1}^{v_2} p\,dv - l_{23} - l_{12} = 0, \quad . \quad . \quad . \quad (138)$$

and

$$p_1v_1 + \int_{v_1}^{v_2} p\,dv - p_2v_2 = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (139)$$

But

$$\int_{v_1}^{v_2} p\,dv = p_2v_2 - p_1v_1 - \int_{p_1}^{p_2} v\,dp.$$

Hence from equation (139):

$$\int_{p_1}^{p_2} v\,dp = 0$$

or

$$p_1 = p_2,$$

the result we set out to prove.

Also as the vapour pressures over the ice and water are the same, $v_1 = v_2$, and therefore from equation (138):

$$l_{13} = l_{12} + l_{23}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (140)$$

or at the triple point the latent heat of change of state from solid to vapour is equal to the sum of the latent heats of changes of state from solid to liquid and liquid to vapour.

It is only at the triple point that the three forms of water are able to exist together in a state of equilibrium. This equilibrium is maintained under the pressure exerted by the vapour alone at a temperature very near 0° C. Now at this temperature the vapour pressure of water is something less than 5 mms. of mercury, or nearly one atmosphere less than the pressure which corresponds to a melting-point of ice of 0° C. Consequently the temperature of the triple point is +0·0075° C., as this is the amount by which the ice-point is raised for a decrease in the pressure of one atmosphere. Experiment gives the values 4·579 mm. of mercury and +0·0075° C. as the pressure and temperature of the triple point.

Having proved the existence of a triple point, we shall now proceed to show that the lines PA and PC, Fig. 27, are not continuous. In order to do this it will be sufficient to show that $\left(\frac{dp}{dT}\right)$ has different values at the triple point for the two lines.

Let the solid, liquid, and vapour states be denoted by the suffixes 1, 2, 3, respectively, and μ the difference of specific volumes, such that μ_{12} is the difference of specific volumes in the liquid and solid states, and l_{12} is the latent heat of change of state from solid to liquid. The Clapeyron equation can then be written for the three changes:

$$\left(\frac{dp}{dT}\right)_{12}=\frac{l_{12}}{T\mu_{12}},\quad \left(\frac{dp}{dT}\right)_{23}=\frac{l_{23}}{T\mu_{23}},\quad \left(\frac{dp}{dT}\right)_{13}=\frac{l_{13}}{T\mu_{13}}.$$

The difference of slope of the lines PA and PC is given by

$$\left(\frac{dp}{dT}\right)_{13}-\left(\frac{dp}{dT}\right)_{23}=\frac{1}{T}\left\{\frac{l_{13}}{\mu_{13}}-\frac{l_{23}}{\mu_{23}}\right\}. \quad . \quad . \quad (141)$$

Now at the triple point

$$\mu_{13}=\mu_{12}+\mu_{23},$$

and by equation (140):

$$l_{13}=l_{12}+l_{23}.$$

Hence, substituting these values in equation (141), we have:

$$\left(\frac{dp}{dT}\right)_{13}-\left(\frac{dp}{dT}\right)_{23}=\frac{l_{12}\mu_{23}-l_{23}\mu_{12}}{T\mu_{23}(\mu_{12}+\mu_{23})},$$

$$\doteq\frac{l_{12}}{T\mu_{23}},$$

as μ_{12} is small in comparison with μ_{23}. All the quantities on the right-hand side of this equation are positive, so that at the triple point the slope of the line PC is greater than that of the line PA.

71. Integration of the Clapeyron Equation.—By integration of the Clapeyron equation an equation connecting the pressure of a saturated vapour with temperature can be obtained.

We can identify the constant *b* of Callendar's equation with the volume occupied by the substance in the liquid form, and write the equation:

$$v_2 - v_1 = \frac{RT}{p} - c.$$

Neglecting c, which is a small quantity in comparison with the other terms, this value for $(v_2 - v_1)$ can be substituted in the Clapeyron equation, which then becomes:

$$\frac{l}{T} = \frac{RT}{p} \cdot \left(\frac{dp}{dT}\right)_v,$$

or

$$\frac{dp}{p} = \frac{l}{R}\frac{dT}{T^2}. \qquad (142)$$

Integrating this equation, assuming l constant, we have:

$$\log p = A + \frac{B}{T}.$$

This simple equation for the pressure of a saturated vapour was proposed by Young in 1820, from a consideration of experimental results.

If we have two substances having the same vapour pressure at temperatures T_1 and T_2 respectively, we obtain:

$$\log p = A_1 + \frac{B_1}{T_1} = A_2 + \frac{B_2}{T_2},$$

and hence

$$\frac{T_1}{T_2} = \frac{1}{B_2}\{B_1 + (A_1 - A_2)T_1\}.$$

The equation has been used in this form by Ramsay and Young* to deduce the vapour pressures of various substances. These pressures were obtained from measurements of the vapour pressure of a standard substance, and two observations with the particular substance to determine the constants.

A more exact equation can be obtained by taking into account the variation of the latent heat with temperature. For a small range this can be considered as approximately linear. Thus, writing

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* Ramsay and Young, *Phil. Mag.* (1887).

$$l = M + NT,$$

where M and N are constants, and substituting this value for l in equation (142) we have, on integration:

$$\log p = A + \frac{B}{T} + C \log T,$$

an equation proposed by Kirchhoff in 1858, and independently by Rankine in 1866.*

72. The Latent Heat Equation.—We can obtain a general expression for the latent heat of a liquid in terms of the temperature in the following manner.

Let us start with one gram of the liquid at a temperature T_1 and vaporize it at this temperature. Denoting the latent heat at T_1 by l_{T_1} the change of internal energy is:

$$l_{T_1} - p_1 v_1,$$

where p_1 is the vapour pressure at the temperature T_1 and v_1 the specific volume of the vapour. Assuming that the vapour behaves as a perfect gas, this may be written:

$$l_{T_1} - RT_1.$$

If the vapour is now heated at constant volume to a temperature T_2 the internal energy will increase by a further amount:

$$\int_{T_1}^{T_2} c_v \, dT,$$

so that the total change in internal energy is:

$$l_{T_1} - RT_1 + \int_{T_1}^{T_2} c_v \, dT.$$

The change in internal energy between the temperatures T_1 and T_2 may be obtained in a different manner. First heat the liquid at constant pressure from T_1 to T_2, and then allow it to vaporize at the higher temperature. If the small amount of work done against the external pressure in heating the liquid is neglected the change in internal energy is:

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* See also Laby, *Phil. Mag.*, **16**, 789 (1908), and Egerton, *Phil. Mag.*, **39**, 1 (1920).

$$l_{T_2} - RT_2 + \int_{T_1}^{T_2} c_p^l dT,$$

where c_p^l is the specific heat of the liquid.

Now we have assumed that the vapour obeys the perfect gas laws, so that the change in internal energy is independent of the volume. Hence the two expressions for the change of internal energy must be equal. Therefore

$$l_{T_1} - RT_1 + \int_{T_1}^{T_2} c_v dT = l_{T_2} - RT_2 + \int_{T_1}^{T_2} c_p^l dT,$$

or

$$l_{T_2} = l_{T_1} + \int_{T_1}^{T_2} c_p dT - \int_{T_1}^{T_2} c_p^l dT,$$

where $c_v + R$ has been replaced by c_p. To obtain the general expression put $T_1 = 0$ and $T_2 = T$. The equation then becomes:

$$l_T = l_0 + \int_0^T (c_p - c_p^l) dT, \quad . \quad . \quad . \quad (143)$$

l_0 corresponding to the latent heat at the absolute zero of temperature. We cannot determine l_0 by experiment, but it is sufficient for our purposes to regard it as a constant defined by equation (143). It is obvious that an equation similar to (143) will give the latent heat of change of state from solid to vapour, c_p^l in that case being the specific heat at constant pressure of the solid.

The above equation gives the value of the latent heat in terms of the specific heats of two states, *i.e.* vapour and either solid or liquid. In many cases in order to raise the temperature of the substance from the lower to the higher temperature it would be necessary to start with it in the solid form at the lower temperature, heat it to T′ where liquefaction would take place, and then heat the liquid to the higher temperature, where it is vaporised. With the same limitations as before, the expression for the latent heat of vaporisation of the liquid at the temperature T becomes

$$l^l_T = l_0 + \int_0^T c_p dT - l_f - \int_0^{T'} c_p^s dT - \int_{T'}^T c_p^l dT$$

where l_f is the latent heat of fusion at the temperature T', c_p^s and c_p^l the specific heats of the solid and liquid respectively, and c_p that of the vapour.

If the value of l given by equation (143) is substituted in equation (142), we have:

$$\frac{dp}{p} = \frac{l_0}{R}\frac{dT}{T^2} + \frac{dT}{RT^2}\int_0^T (c_p - c_p^l)dT,$$

or upon integration:

$$\log p = -\frac{l_0}{RT} + \int_0^T \frac{dT}{RT^2}\int_0^T (c_p - c_p^l)dT + i, \qquad (144)$$

where i is an integration constant known as the chemical constant. This equation is a general expression for the vapour pressure of a substance in terms of the temperature. The assumptions made in the proof must be borne in mind when using this equation, it being strictly applicable only in the case of a vapour which behaves as a perfect gas.

For most practical purposes it is convenient to use common logarithms and express pressures in atmospheres. Further it is convenient to divide the specific heat of the vapour into two parts $(c_p)_0$ and $(c_p)_1$, of which $(c_p)_0$ is constant over the temperature range considered and $(c_p)_1$ a variable part. Equation (144) may then be written

$$\log_{10} p = \frac{-l_0}{2{\cdot}3026RT} + \frac{(c_p)_0}{R}\log_{10} T + \frac{1}{2{\cdot}3026}\int_0^T \frac{dT}{RT^2}\int_0^T (c_p)_1 - c_p^l)dT + C,$$

where C is sometimes called the conventional chemical constant.

CHAPTER VIII

THE EQUILIBRIUM OF SYSTEMS*

73. Conditions of the Possibility of a Transformation. —It has been shown in Chapter III that if a substance is transformed from a state A to a state B then in general:

$$\sum_A^B \frac{\delta \mathbf{q}}{T} + \mathbf{S}_A - \mathbf{S}_B < 0.$$

In the limiting case when the process by which the substance is transferred from the state A to the state B is reversible, $\sum_A^B \frac{\delta \mathbf{q}}{T}$ will be the change of entropy of the substance and the inequality sign will be replaced by one of equality. Consequently for all possible transformations from the state A to the state B we must have:

$$\sum_A^B \frac{\delta \mathbf{q}}{T} \leqslant \mathbf{S}_B - \mathbf{S}_A \quad . \quad . \quad . \quad . \quad . \quad . \quad (145)$$

Any transformation which would make the summation of greater value than the change of entropy between the two states could not possibly take place; when the value of the summation is equal to the change of entropy, we may conclude that the path over which the transformation takes place is reversible.

The inequality (145) is, therefore, the condition of the possibility of a transformation from the state A to the state B. For an infinitesimal change it becomes:

$$\delta \mathbf{q} \leqslant T d\mathbf{S}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (146)$$

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* In this and the following chapters bold Roman type will be used to denote the properties of an arbitrary mass. Thus **E** means the total internal energy of a system, whereas *E* is the internal energy per gram. Similarly with the other symbols.

When the system under consideration is isolated $\delta \mathbf{q}$ is zero, and the condition of possibility of a transformation reduces to:

$$T d\mathbf{S} \geqslant 0, \qquad (147)$$

or all possible irreversible changes in the system are accompanied by an increase in entropy. The spontaneous changes which occur in nature are irreversible processes, and hence it follows from this last inequality that an isolated system will be in stable equilibrium when the entropy is a maximum, for it is then impossible for this quantity to increase, and therefore no change in the system can take place.

Since in all cases the heat given to a system must be equal to the change in internal energy together with the external work done, on substitution of the inequality (146) in the mathematical expression for the first law of thermodynamics, equation (14), we have:

$$T d\mathbf{S} \geqslant d\mathbf{E} + p d\mathbf{v} \qquad (149)$$

The conditions of possibility of a transformation can be expressed in terms of either of the thermodynamic potentials. From the definition of the thermodynamic potential at constant volume we have:

$$\mathbf{A} = \mathbf{E} - T\mathbf{S},$$

and differentiating:

$$d\mathbf{A} = d\mathbf{E} - T d\mathbf{S} - \mathbf{S} dT,$$

and using equation (149):

$$d\mathbf{A} \leqslant -p d\mathbf{v} - \mathbf{S} dT. \qquad (150)$$

Similarly for the thermodynamic potential at constant pressure:

$$d\mathbf{G} \leqslant \mathbf{v} dp - \mathbf{S} dT. \qquad (151)$$

In an isothermal process for which the volume is constant both dT and $d\mathbf{v}$ are zero. Hence from equation (150) for any isothermal change at constant volume:

$$d\mathbf{A} \leqslant 0$$

Similarly from equation (151) for an isothermal change at constant pressure:

$$d\mathbf{G} \leqslant 0.$$

We have now deduced the conditions for the possibilities of changes in a system in the three cases which are of practical importance.

(i) In an isolated system the entropy cannot decrease.

(ii) In an isothermal system, whose volume is constant, the function **A** cannot increase.

(iii) In an isothermal system, the pressure remaining constant, the function **G** cannot increase.

From (ii) and (iii) it follows that if **A** and **G** are at minimum values no transformation of the system is possible, and in each case, under the specified conditions, the system will be in stable equilibrium. In rational mechanics a system is in stable equilibrium when the potential energy is at a minimum, and it is by analogy that **A** and **G** have been called the thermodynamic potentials.

74. Equilibrium between Three States of the Same Substance.—The general conditions for equilibrium between the three states of a substance can be deduced by making use of the above results. Suppose we have a total mass $\mathbf{M}$ of a substance, $\mathbf{M}_1$ existing in the first state, $\mathbf{M}_2$ in the second, and $\mathbf{M}_3$ in the third. The total mass, volume, and internal energy of the system are given by:

$$\left.\begin{aligned} \mathbf{M} &= \mathbf{M}_1 + \mathbf{M}_2 + \mathbf{M}_3 \\ \mathbf{v} &= \mathbf{M}_1 v_1 + \mathbf{M}_2 v_2 + \mathbf{M}_3 v_3 \\ \mathbf{E} &= \mathbf{M}_1 E_1 + \mathbf{M}_2 E_2 + \mathbf{M}_3 E_3 \end{aligned}\right\} \quad . \quad . \quad . \quad (152)$$

where v_1, v_2, v_3, and E_1, E_2, E_3 are the specific volumes and internal energies in the three states respectively. (The notation of suffixed symbols to denote the three states will be used for the other symbols as required.) These equations represent the external conditions, and for an isolated system whose volume is kept constant $\mathbf{M}$, $\mathbf{E}$, and $\mathbf{v}$ will be constant.

The total entropy of the system is given by:

$$\mathbf{S} = \mathbf{M}_1 S_1 + \mathbf{M}_2 S_2 + \mathbf{M}_3 S_3,$$

which upon differentiation becomes:

$$d\mathbf{S} = \Sigma \mathbf{M}_1 dS_1 + \Sigma S_1 d\mathbf{M}_1. \quad . \quad . \quad . \quad (153)$$

Now for a simple substance existing in one state only:

$$T_1 dS_1 = dE_1 + p_1 dv_1,$$

or

$$dS_1 = \frac{dE_1}{T_1} + \frac{p_1}{T_1} dv_1.$$

Hence

$$\Sigma \mathbf{M}_1 dS_1 = \Sigma \mathbf{M}_1 \frac{dE_1}{T_1} + \Sigma \mathbf{M}_1 \frac{p_1 dv_1}{T_1}.$$

Therefore equation (153) on substitution becomes:

$$d\mathbf{S} = \Sigma \mathbf{M}_1 \frac{dE_1}{T_1} + \Sigma \mathbf{M}_1 \frac{p_1 dv_1}{T_1} + \Sigma S_1 d\mathbf{M}_1. \quad . \quad . \quad (154)$$

The variations involved in this equation are not independent of one another, but are constrained by the external conditions of equations (152). These equations on differentiation give:

$$\left.\begin{aligned} &\Sigma d\mathbf{M}_1 = 0 \\ &\Sigma \mathbf{M}_1 dv_1 + \Sigma v_1 d\mathbf{M}_1 = 0 \\ &\Sigma \mathbf{M}_1 dE_1 + \Sigma E_1 d\mathbf{M}_1 = 0 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (155)$$

Substituting in equation (154) the values of $d\mathbf{M}_2$, dv_2, and dE_2 from equations (155), we have:

$$\begin{aligned} d\mathbf{S} = &\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\mathbf{M}_1 dE_1 - \left(\frac{1}{T_2} - \frac{1}{T_3}\right)\mathbf{M}_3 dE_3 \\ &+ \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)\mathbf{M}_1 dv_1 - \left(\frac{p_2}{T_2} - \frac{p_3}{T_3}\right)\mathbf{M}_3 dv_3 \\ &+ \left\{S_1 - S_2 - \frac{E_1 - E_2}{T_2} - \frac{p_2(v_1 - v_2)}{T_1}\right\} d\mathbf{M}_1 \\ &- \left\{S_2 - S_3 - \frac{E_2 - E_3}{T_2} - \frac{p_2(v_2 - v_3)}{T_2}\right\} d\mathbf{M}_3, \quad . \quad (156) \end{aligned}$$

in which the variations are now independent of one another.

Now we have already seen that the condition for equilibrium in an isolated system is that the entropy shall be at a maximum. That is:

$$d\mathbf{S} = 0,$$

and

$$d^2\mathbf{S} = \text{some negative quantity.}$$

Hence for the first of these conditions to be fulfilled the coefficients in equation (156) must separately vanish as they are all independent, the change of entropy only being zero for any change in the six independent variables if the coefficients are each zero. Hence

$$\left.\begin{aligned} T_1 = T_2 = T_3 = T \text{ (say)} \\ p_1 = p_2 = p_3 = p \text{ (say)} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (157)$$

$$S_1 - S_2 = \frac{E_1 - E_2 + p(v_1 - v_2)}{T},$$

$$S_2 - S_3 = \frac{E_2 - E_3 + p(v_2 - v_3)}{T}.$$

The last two equations by the definition of the thermodynamic potential at constant pressure reduce to:

$$G_1 = G_2 = G_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (158)$$

Thus we see that for three states of a substance to be co-existent, the pressure, temperature, and thermodynamic potential at constant pressure must be the same for the three states. These are the conditions for a triple point.

We can now proceed to examine whether the solution given by equations (157) and (158) gives a maximum value of the entropy. Differentiating equation (156) as it stands, and simplifying by means of equations (158), (157), and (152), we have finally:

$$Td^2\mathbf{S} = -\Sigma\mathbf{M}_1 dS_1 dT_1 + \Sigma\mathbf{M}_1 dp_1 dv_1. \quad . \quad . \quad (159)$$

Now

$$dS = \left(\frac{dS}{dv}\right)_T dv + \left(\frac{dS}{dT}\right)_v dT,$$

$$= \left(\frac{dp}{dT}\right)_v dv + \frac{c_v}{T} dT,$$

and

$$dp = \left(\frac{dp}{dT}\right)_v dT + \left(\frac{dp}{dv}\right)_T dv.$$

Substituting these values in equation (159) this becomes:

$$Td^2\mathbf{S} = -\Sigma\mathbf{M}_1\left\{\frac{(c_v)_1}{T}dT_1{}^2 - \left(\frac{dp_1}{dv_1}\right)_T dv_1{}^2\right\}.$$

If $(c_v)_1$, $(c_v)_2$, $(c_v)_3$ are all positive, and $\left(\frac{dp_1}{dv_1}\right)_T$, etc., all negative, as they are for all known substances, $d^2\mathbf{S}$ must be a negative quantity. Hence the solution obtained above corresponds to a maximum value of the entropy, and therefore a state of stable equilibrium.

75. Alternative Deduction of Clapeyron's Equation.—

If we consider only two states of a substance in equilibrium with one another we have, from the results of the foregoing section,

$$G_1 = G_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (160)$$

the suffixes referring to the first and second states respectively. Writing this in full:

$$E_1 - TS_1 + pv_1 = E_2 - TS_2 + pv_2,$$

or

$$T(S_2 - S_1) = E_2 - E_1 + p(v_2 - v_1).$$

Now in a change of state the increase in entropy is the latent heat divided by the absolute temperature, and hence

$$l = E_2 - E_1 + p(v_2 - v_1).$$

The equation (160) applies to a change of state at the temperature T. At a different temperature, say $T + dT$, both G_1 and G_2 will have increased, but in order that equation (160) may still be true these increments must be equal. Hence

$$dG_1 = dG_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (161)$$

For a simple substance:

$$dG = vdp - SdT,$$

and therefore expanding equation (161) we obtain:

$$v_1dp - S_1dT = v_2dp - S_2dT,$$

or

$$S_2 - S_1 = (v_2 - v_1)\frac{dp}{dT}.$$

Substituting as before for $S_2 - S_1$, this becomes:

$$\frac{l}{T} = (v_2 - v_1)\frac{dp}{dT},$$

which is Clapeyron's equation.

76. The Phase Rule.—So far we have only studied the equilibrium of systems which consist of a single substance, which may, however, exist in various states of aggregation. For instance, water can exist in the three states: solid, liquid, and vapour; each of these states is known as a phase. In extending the results we have obtained to the general case of equilibrium in a system, any part of the system which is homogeneous throughout is called a phase. A phase is always bounded by a surface, and is mechanically separable from the other parts of the system. There may be several liquid or solid phases present in a system, but as two gases in contact with one another, but not mixed, are never in equilibrium, there can never be more than one gaseous phase. A phase need not be continuous, although of course the gaseous and liquid phases usually are; a solid is most often present as a series of discontinuous fragments, but any solid of homogeneous composition, no matter into what number of pieces it may be divided, constitutes but a single phase. Similarly, if a liquid phase is broken into droplets by agitation, the number of phases is not increased.

Besides the phases, the system is characterised by the number of components present. This is defined as the smallest number of independently variable constituents by means of which the composition of each phase may be mathematically expressed. The number of components is most commonly deduced from a knowledge of the physical or chemical changes which the system undergoes. A few examples will make the method clear.

If the system consists of water only, there is one component however many phases may be present. Also, if partial or complete dissociation has occurred, the number of components remains unaltered.

The system nitric oxide, nitrogen, oxygen, may be either a two- or three-component system. If the temperature is so low that no chemical combination takes place, then the number of components is obviously three, but if the temperature is raised, so that the chemical reaction

$$N_2 + O_2 \rightleftarrows 2NO$$

takes place, the number of components is two. This is because starting with a mixture of oxygen and nitrogen the nitric oxide can be formed within the system itself.

Again, consider the decomposition of calcium carbonate by heat. In this case there are two solid phases, namely, $CaCO_3$ and CaO, and the gaseous phase CO_2. Using any two of these three substances the composition of each of the three phases may be expressed in the usual terms of percentage by weight, or in terms of other units. This, then, is a two-component system.

Let us consider the equilibrium of a system which has C components, the masses of which, $\mathbf{M}_1$, $\mathbf{M}_2$, . . . $\mathbf{M}_c$, are given. If there are P phases, i.e. P physically homogeneous parts of the system, the masses of the various components in the different phases will be:

$$\begin{array}{l} \mathbf{M}_1{}', \mathbf{M}_2{}', \ \ldots \ \mathbf{M}_c{}', \\ \mathbf{M}_1{}'', \mathbf{M}_2{}'', \ldots \ \mathbf{M}_c{}'', \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ \mathbf{M}_1{}^P, \mathbf{M}_2{}^P, \ \ldots \ \mathbf{M}_c{}^P, \end{array}$$

where the superscripts refer to the number of phases, and the subscripts to components.

The total thermodynamic potential of the whole system will be the sum of P terms, each of which refers to a single phase. Thus:

$$\mathbf{G} = \mathbf{G}' + \mathbf{G}'' + \ldots + \mathbf{G}^P.$$

Now the expression for the thermodynamic potential of the first phase is:

$$\mathbf{G}' = \mathbf{E}' - T\mathbf{S}' + p\mathbf{v}'.$$

All the quantities occurring on the right-hand side of this equation are completely determined by the masses of the various components in the phase, together with the pressure and temperature which we shall suppose constant. We have similar expressions for the thermodynamic potentials of the other phases, and these also are completely specified in terms of the masses of the components and the pressure and temperature.

Let us now inquire as to how the thermodynamic potential depends upon the masses of the components. We know that if the mass of each component in a certain phase were increased in a fixed proportion, the thermodynamic potential of the whole phase would be increased in the same proportion, for the total internal energy, entropy, and volume are each proportional to the mass. Suppose, then, that the masses of the components in the first phase are all increased in the ratio $(1 + \epsilon) : 1$, where ϵ is a small quantity. The change $\varDelta\mathbf{G}'$ in $\mathbf{G}'$ is given by:

$$\begin{aligned}\varDelta \mathbf{G}' &= \frac{d\mathbf{G}'}{d\mathbf{M}_1'}\varDelta\mathbf{M}_1' + \frac{d\mathbf{G}'}{d\mathbf{M}_2'}\varDelta\mathbf{M}_2' + \ . \ . \ . + \frac{d\mathbf{G}'}{d\mathbf{M}_c'}\varDelta\mathbf{M}_c', \\ &= \epsilon\left\{\frac{d\mathbf{G}'}{d\mathbf{M}_1'}\mathbf{M}_1' + \frac{d\mathbf{G}'}{d\mathbf{M}_2'}\mathbf{M}_2' + \ . \ . \ . + \frac{d\mathbf{G}'}{d\mathbf{M}_c'}\mathbf{M}_c'\right\}.\end{aligned}$$

But as $\mathbf{G}'$ is increased in the same proportion as the masses of the various components:

$$\varDelta\mathbf{G}' = \epsilon\mathbf{G}',$$

and hence

$$\mathbf{G}' = \frac{d\mathbf{G}'}{d\mathbf{M}_1'}\mathbf{M}_1' + \frac{d\mathbf{G}'}{d\mathbf{M}_2'}\mathbf{M}_2' + \ . \ . \ . \ \frac{d\mathbf{G}'}{d\mathbf{M}_c'}\mathbf{M}_c'. \quad . \quad (162)$$

The differential coefficients in this equation depend only upon the constitution of the phase and not on its total mass, for if $\mathbf{M}_1'$, $\mathbf{M}_2'$ . . . $\mathbf{M}_c'$ were all doubled $\mathbf{G}'$ would also be doubled, the values of the differential coefficients therefore remaining unaltered.

Since these differential coefficients are determined by the specific properties of the phase it is useful and convenient to denote them by a special symbol. For this purpose the symbol μ is usually adopted and, following Gibbs, is named the chemical potential. Thus μ_1' is the chemical potential of the first component in the first phase. It should be particularly noticed that the chemical potentials are functions of the pressure, temperature and compositions of the phase. We may now rewrite equation (162) in the form

$$\mathbf{G}' = \mathbf{M}_1'\mu_1' + \mathbf{M}_2'\mu_2' + \ldots \mathbf{M}_c'\mu_c' \quad . \quad . \quad . \quad . \qquad (162a)$$

The condition for equilibrium in a system at constant pressure and temperature is that **G** should be at a minimum value. Hence

$$d\mathbf{G} = d\mathbf{G}' + d\mathbf{G}'' + \ldots d\mathbf{G}^P = 0. \quad . \quad . \quad . \qquad (163)$$

We have already seen that at constant pressure and temperature the only way in which **G** for any phase can vary is by the variation of the masses of the different components in that phase. Hence differentiating equation (162*a*) and the others like it for the other phases, and substituting in equation (163), the condition for equilibrium becomes:

$$\begin{aligned} &\mu_1'\,d\mathbf{M}_1' + \mu_2'\,d\mathbf{M}_2' + \ldots + \mu_c'\,d\mathbf{M}_c' \\ &+ \mu_1''\,d\mathbf{M}_1'' + \mu_2''\,d\mathbf{M}_2'' + \ldots + \mu_c''\,d\mathbf{M}_c'' \\ &+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \\ &+ \mu_1^P\,d\mathbf{M}_1^P + \mu_2^P\,d\mathbf{M}_2^P + \ldots + \mu_c^P\,d\mathbf{M}_c^P = 0 \quad . \qquad (164) \end{aligned}$$

If the variation of the masses was entirely arbitrary, this equation could only be satisfied if the coefficients of each of the variations were zero. We are, however, provided with another set of equations connecting these variations, for the total mass of any component in the system being constant, the sum of the variations of the masses of the component in the different phases must be zero. That is:

$$\left.\begin{aligned} d\mathbf{M}_1' + d\mathbf{M}_1'' + d\mathbf{M}_1''' + \ldots + d\mathbf{M}_1^P &= 0 \\ d\mathbf{M}_2' + d\mathbf{M}_2'' + d\mathbf{M}_2''' + \ldots + d\mathbf{M}_2^P &= 0 \\ . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad &. \\ d\mathbf{M}_c' + d\mathbf{M}_c'' + d\mathbf{M}_c''' + \ldots + d\mathbf{M}_c^P &= 0 \end{aligned}\right\} \quad . \qquad (165)$$

Multiplying equations (165) by $\lambda_1, \lambda_2, \ldots \lambda_c$, adding them to equation (164) and equating to zero the coefficients of the various differentials, we have:

$$\mu_1' + \lambda_1 = 0\,, \quad \mu_1'' + \lambda_1 = 0, \quad \text{etc.}$$
$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$
$$\mu_c' + \lambda_c = 0\,, \quad \mu_c'' + \lambda_c = 0, \quad \text{etc.}$$

Hence the necessary and sufficient condition for the vanishing of the left-hand side of equation (164) is:

$$\left.\begin{array}{l} \mu_1' = \mu_1'' = \ldots = \mu_1^P \\ \mu_2' = \mu_2'' = \ldots = \mu_2^P \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ \mu_c' = \mu_c'' = \ldots = \mu_c^P \end{array}\right\} \quad \ldots \ldots \quad (166)$$

These equations give the condition for the thermodynamic equilibrium of the system.

To specify the system under consideration completely we have to know a number of variables which can be arrived at in the following manner. Consider any one phase. If the masses of $(C - 1)$ components of the phase contained in unit mass of the phase are known, the relative proportions of the masses of all the components are determined. As there are P phases, this gives $P(C - 1)$ variables to be specified in order to determine the relative proportions of the components in each of the phases. In addition the quantities in equations (166) depend upon the pressure and temperature, so that in all there are $P(C - 1) + 2$ variables to be fixed in order to specify the system completely. Equations (166) provide $(P - 1)$ independent equations for each component, and therefore $C(P - 1)$ equations which must be satisfied if the whole system is to be in thermodynamic equilibrium. That is, we have only $C(P - 1)$ equations to determine the $P(C - 1) + 2$ variables which specify the system, and therefore there will be a number of variables which may be arbitrarily adjusted. The number of variables which may be arbitrarily varied is termed the number of *Degrees of Freedom* of the system. Denoting this by F we have:

$$F = P(C - 1) + 2 - C(P - 1),$$

or

$$F = C - P + 2. \quad . \quad . \quad . \quad . \quad . \quad (167)$$

This is the *Phase Rule* discovered by Willard Gibbs,* and now amply tested and verified by a wealth of experimental work on physical and chemical equilibrium.

77. The Use of the Phase Rule.—As illustrations of the use of the phase rule we will consider a few typical simple cases.

(i) *Non-Variant Systems.*—Let us suppose that there are no degrees of freedom; such a system is called non-variant. In the case of water, one component, we have by equation (167):

$$P = 3.$$

That is, the three phases are coexistent and in equilibrium. As the system is non-variant, neither the pressure nor the temperature can be arbitrarily varied; such a system exists therefore at one definite pressure and temperature only. We have already seen that in the case of water the solid, liquid, and vapour can only exist together in equilibrium at 0·0075° C. and at a pressure of 4·579 mm. of mercury. It might be noticed in passing that experiments by Bridgman† indicate that the nature of the solid phase of water changes under high pressures, altogether five different forms of ice being obtained. These different forms each constitute different phases, and give rise to other triple points.

(The ordinary fixed point of 0° C. corresponds to an equilibrium point of a multi-component system where the phases are ice, aqueous solution of air, and vapour phase, the total pressure being one atmosphere. This system is not non-variant.)

Sulphur exists in two well-defined crystalline modifications, rhombic and monoclinic sulphur. These have a transition temperature, 96° C., at which they are in equilibrium. For this substance there are three triple points. Fig. 29 shows how these occur.

In general, a non-variant system with C components forms a

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* Gibbs, *Collected Works*, vol. i, p. 55 *et seq.*

† Bridgman, *Proc. Amer. Acad.*, **47**, 441 (1912).

$(C + 2)$ple point as the number of phases is $(C + 2)$, and they are coexistent.

(ii) *Univariant Systems.*—For a univariant system we have :

$$P = C + 1,$$

or C components form $(C + 1)$ phases. Considering again the case of water, two phases can exist in equilibrium with one variable being arbitrarily adjustable. That is, if the temperature is fixed the pressure will have a unique value. This may be seen by reference to the curves in Fig. 27. If the pressure is varied at this chosen temperature the conditions for equilibrium will no longer be fulfilled, and one of the phases will go out of existence.

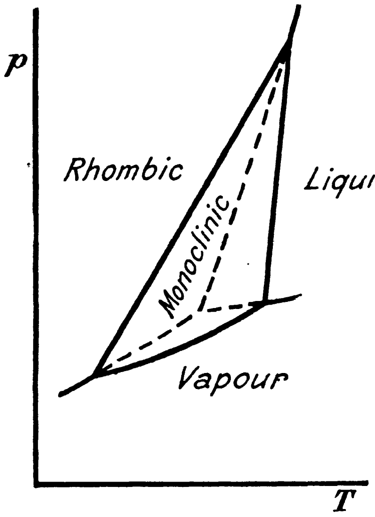

Fig. 29.

Triple Points for Sulphur.

Another example of a univariant system is a solution of a salt, say $NaCl$, in contact with solid $NaCl$ and the vapour of the solvent. In this case we have a two-component system and three phases, the system being univariant. If the temperature is fixed the vapour pressure and the concentration of the solution will take up definite values. In other words, the vapour pressure and the concentration are functions of the temperature alone when the system is in equilibrium.

(iii) *Divariant System.*—In this case the number of phases is equal to the number of components, i.e.:

$$P = C.$$

If the system has only one component there is also only one phase. The pressure and temperature can in this case be varied arbitrarily within certain limits, the range of which the laws of thermodynamics alone are not sufficient to define.

An example of a divariant system of importance in the study of chemistry is a mixture of two liquids which are miscible in all proportions, e.g. water and ethyl alcohol. This is a two-component system, and if the vapour phase is present, divariant. Supposing the temperature to be fixed, then the vapour pressure will vary only with the concentration, and this variation can be represented by a curve.

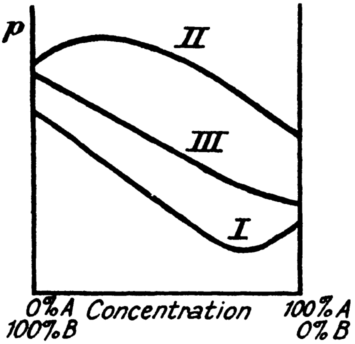

FIG. 30.

The general types of vapour pressure-concentration curves for mixtures of two liquids A and B are shown in Fig. 30. In practical laboratory work distillation is most often performed at constant pressure and not constant temperature. In general, the vapour phase has a different composition from the liquid phase, and during distillation the composition of the liquid phase alters so as to reduce the vapour pressure. Hence the boiling-point rises during distillation. The composition of the distillate and of the residue depends upon the form of the pressure-concentration curve. For a curve such as I, Fig. 30, the final residue will be the mixture with the minimal vapour pressure, whilst if the distillate is fractionally distilled a sufficient number of times the final product will be one of the pure solvents. This solvent will be the one that was present originally in a larger proportion than that required by the mixture of minimum vapour pressure. In the case of a mixture giving a curve such as II, the residue will be one of the pure solvents, and the final distillate after repeated fractionation will be the mixture corresponding to the maximum vapour pressure. It is only in the case of a mixture giving a curve similar to III that it is possible completely to separate the two liquids by repeated distillations.

78. Thermodynamic Surfaces.—Up to the present when we have required to represent the state of a body diagrammatically, we have used a plane diagram, such as a $p - v$ diagram, or a $T - S$ diagram; in each case only two thermodynamic properties of the body are represented. Each point on such a diagram corresponds to some perfectly definite state of the body or system under consideration, but a curve is traced out only when the indicator point is made to move in such a manner that some fixed condition is fulfilled. For instance, if the condition is that the temperature is constant, isothermals are traced, or entropy constant, then adiabatics are traced. If any pair of the eight quantities p, v, T, S, E, H, A, G be taken as rectangular coordinates for a plane diagram, then every point in the plane will represent a definite state of the body for which the remaining six quantities have definite values, as each is a function of the state of the substance only. Consequently at each point in the plane diagram a perpendicular can be erected whose length is proportional to the value of any of the thermodynamic quantities which has not been chosen as one of the coordinates in the plane diagram. The end of this perpendicular as it moves from point to point over the plane will trace out a surface of some description, the shape of which will depend upon the nature of the substance. That is, if any three of the quantities p, v, T, S, E, H, A, G be taken as the rectangular coordinates of a point P in space, then as the substance passes through its various equilibrium conditions the point P will trace out a surface whose geometrical properties will depend upon the nature of the substance. A large number of different surfaces can be obtained by choosing different quantities as the coordinates, but we shall only consider here the surface obtained by taking v, S, and E as the rectangular coordinates. This surface has been studied in detail by Willard Gibbs,* who originated this method of representation.

It must be noted that of the three mutually perpendicular planes corresponding to zero volume, zero entropy, and zero internal energy, the plane of zero volume is alone definite, as both of the other quantities include an arbitrary constant. The planes of zero entropy and zero internal energy are chosen to represent the conditions under which the substance is arbitrarily assumed to have zero values for these quantities; then all the points on the surface will correspond to a definite condition of the substance. Consider an arbitrary mass **M**. As a definite surface is traced out by the variation of the three quantities **v**, **S**, and **E** there will be a connection between them of the form:

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* Gibbs, *Collected Works*, vol. i, p. 33.

$$\mathbf{E} = f(\mathbf{v}, \mathbf{S}), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (168)$$

where f is some undetermined function of the independent variables **v** and **S**. From the equation:

$$Td\mathbf{S} = d\mathbf{E} + pd\mathbf{v},$$

we have:

$$T = \left(\frac{d\mathbf{E}}{d\mathbf{S}}\right)_v \text{ and } p = -\left(\frac{d\mathbf{E}}{d\mathbf{v}}\right)_S. \quad . \quad . \quad (169)$$

Hence the temperature and pressure at any point on the surface are determined by the inclination of the tangent plane at this point to the planes $\mathbf{v} = 0$ and $\mathbf{S} = 0$.

79. Condition of Stability.—The equation of the tangent plane to the surface:

$$\mathbf{E} = f(\mathbf{v}, \mathbf{S}),$$

at the point $\mathbf{v}_1$, $\mathbf{S}_1$, $\mathbf{E}_1$, is:

$$(\mathbf{v} - \mathbf{v}_1)\frac{df}{d\mathbf{v}} + (\mathbf{S} - \mathbf{S}_1)\frac{df}{d\mathbf{S}} + (\mathbf{E} - \mathbf{E}_1) = 0,$$

and hence by substitution from equations (168) and (169) we find the equation of the tangent plane to the thermodynamic surface at the point $\mathbf{v}_1$, $\mathbf{S}_1$, $\mathbf{E}_1$, is:

$$(\mathbf{v} - \mathbf{v}_1)(-p_1) + (\mathbf{S} - \mathbf{S}_1)T_1 - (\mathbf{E} - \mathbf{E}_1) = 0. \qquad (170)$$

This is a plane parallel to the plane:

$$\mathbf{E} = -p_1\mathbf{v} + T_1\mathbf{S}. \quad . \quad . \quad . \quad . \quad . \qquad (171)$$

To find the positions on the thermodynamic surface which correspond to stable equilibrium we imagine the point P_1, Fig. 31, to be a state of equilibrium, and P_2 another neighbouring state on the surface. Draw a line parallel to the axis O E from P_2 to meet the tangent plane to the thermodynamic surface at P_1, so that the line meets the plane in N.

The value of $\mathbf{E}$ for the point N is obtained by putting $\mathbf{v} = \mathbf{v}_2$ and $\mathbf{S} = \mathbf{S}_2$ in equation (170).

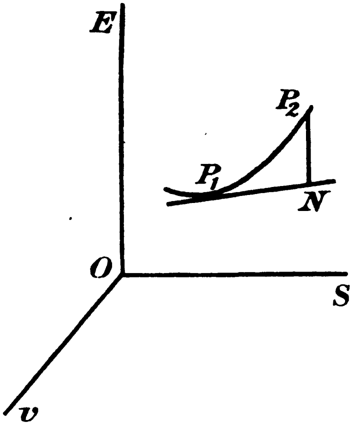

FIG. 31.

Hence at the point N :

$$\mathbf{E} = \mathbf{E}_1 + (\mathbf{v}_2 - \mathbf{v}_1)(-p_1) + (\mathbf{S}_2 - \mathbf{S}_1)T_1,$$

also at the point P_2:

$$\mathbf{E} = \mathbf{E}_2,$$

and therefore:

$$\begin{aligned} P_2N &= \mathbf{E}_2 - \mathbf{E}_1 + p_1(\mathbf{v}_2 - \mathbf{v}_1) - T_1(\mathbf{S}_2 - \mathbf{S}_1), \\ &= \mathbf{G}_2 - \mathbf{G}_1. \end{aligned}$$

The condition of stable equilibrium at constant temperature and pressure is that $\mathbf{G}$ is a minimum. Therefore, if P_1 is a state of stable equilibrium, $\mathbf{G}_2 - \mathbf{G}_1 > 0$, where $\mathbf{G}_2$ is the thermodynamic potential for the point P_2 or any other state near P_1. Consequently $P_2N > 0$ for stable equilibrium, or the thermodynamic surface must be convex to the tangent plane at P_1 and above it.

Thus, by knowing all the tangent planes to the surface parallel to the plane :

$$\mathbf{E} = -p_1\mathbf{v} + T_1\mathbf{S},$$

all the points of contact of these planes with the surface will be states of equilibrium at constant pressure p_1 and constant temperature T_1, the stability depending upon the relation of the surface to the tangent plane at each point.

80. Derived Surfaces.—So far we have limited our attention to the thermodynamic surface of a simple substance existing in a homogeneous state as solid, liquid, or vapour. The surface given by such a substance was termed by Gibbs a primitive surface. The total primitive surface represents the three states of aggregation of a substance, but there are obviously portions of the total surface which represent mixtures of two of the three states and refer to the body when it is changing state. There will be three such portions corresponding respectively to fusion, vaporization, and sublimation; there will also be a further portion of the surface which corresponds to mixtures of the three states. The parts of the surface representing solid, liquid, and vapour will for brevity be referred to as I, II, and III, and the part representing a mixture of solid and liquid will be denoted by (I, II), and similar combinations for the other mixtures.

Every portion of the part I represents a definite condition of the substance when in the solid state, and is bounded partly by a line everywhere along which fusion is about to occur, and partly by a line at every point of which sublimation is about to occur. If there is continuity of state between the solid and liquid states, similar to that between liquid and vapour states, the part I will not be completely enclosed by the lines of fusion and sublimation, but will be joined to the part II by a neck along which no discontinuity of curvature occurs.

Similarly the part II will be bounded by two lines, along one of which solidification is about to occur, and along the other vaporization. These lines will not completely enclose the part II of the surface, for the liquid and vapour states are continuous, and therefore II and III must be united by a portion of the surface presenting no discontinuity.

The part III will be bounded by two lines also. Along one of these condensation to liquid is about to occur, and condensation to solid along the other. Fig. 32 illustrates in perspective the appearance of a surface for a substance which contracts on fusion and expands on vaporization, and for which the internal energy increases progressively as the substance changes state from solid through liquid to vapour, e.g. a substance such as water.

Let us first consider that portion of the surface which represents a mixture of the liquid and vapour. A suffixed symbol will be used to denote the condition on one of the boundary curves, p_{23}, for instance, being the pressure on the liquid when it is about to begin to change into vapour. With this notation the conditions for equilibrium between two states as given by equations (157) and (158) become:—

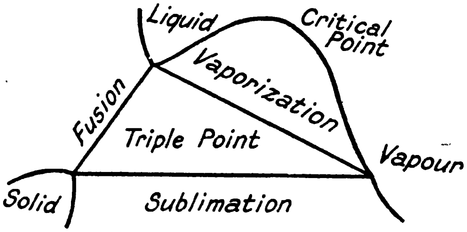

FIG. 32.
A Thermodynamic Surface.

$$\left.\begin{aligned} T_{23} &= T_{32} = T \\ p_{23} &= p_{32} = p \\ \mathbf{S}_{23} - \mathbf{S}_{32} &= \frac{\mathbf{E}_{23} - \mathbf{E}_{32} + p(\mathbf{v}_{23} - \mathbf{v}_{32})}{T} \end{aligned}\right\} \quad . \quad . \quad (172)$$

The equation of the vaporization curve on the thermodynamic surface is given by:

$$\mathbf{v} = \mathbf{v}_{23}, \quad \mathbf{S} = \mathbf{S}_{23}, \quad \mathbf{E} = \mathbf{E}_{23},$$

and the equation of the condensation curve by:

$$\mathbf{v} = \mathbf{v}_{32}, \quad \mathbf{S} = \mathbf{S}_{32}, \quad \mathbf{E} = \mathbf{E}_{32}.$$

These two curves meet in a point the projection of which upon any of the three rectangular planes of coordinates is the critical point. It is obvious that each point on either of these two curves has a corresponding point upon the other, since there are a pair of points on the curves for which the equations (172) are valid.

But the equation to one of the planes the meeting of which with the surface gives equilibrium states is:

$$(\mathbf{v} - \mathbf{v}_{23})(-p_{23}) + (\mathbf{S} - \mathbf{S}_{23})T_{23} - (\mathbf{E} - \mathbf{E}_{23}) = 0.$$

This plane contains the point $(\mathbf{v}_{23}, \mathbf{S}_{23}, \mathbf{E}_{23})$ and the point $(\mathbf{v}_{32}, \mathbf{S}_{32}, \mathbf{E}_{32})$, since these are corresponding points, and also the line joining them. Furthermore, since

$$Td\mathbf{S} = d\mathbf{E} + pd\mathbf{v},$$

the plane must contain also the neighbouring corresponding points:

$$(\mathbf{v}_{23} + d\mathbf{v}_{23}, \quad \mathbf{S}_{23} + d\mathbf{S}_{23}, \quad \mathbf{E}_{23} + d\mathbf{E}_{23})$$

and

$$(\mathbf{v}_{32} + d\mathbf{v}_{32}, \quad \mathbf{S}_{32} + d\mathbf{S}_{32}, \quad \mathbf{E}_{32} + d\mathbf{E}_{32}),$$

and the line joining them. That is, two consecutive generating lines of the surface (II, III) are coplanar, which is the condition of developability of a surface. Thus it follows that the surface (II, III) is developable, and in a similar manner it can be proved that the surfaces (I, II) and (III, I) are also developable.

For a mixture of all three states of a substance equations (152) must be satisfied. Any point with the coordinates:

$$\mathbf{v} = \mathbf{M}\left(\frac{\lambda v_1 + \mu v_2 + \nu v_3}{\lambda + \mu + \nu}\right),$$

$$\mathbf{S} = \mathbf{M}\left(\frac{\lambda S_1 + \mu S_2 + \nu S_3}{\lambda + \mu + \nu}\right),$$

$$\mathbf{E} = \mathbf{M}\left(\frac{\lambda E_1 + \mu E_2 + \nu E_3}{\lambda + \mu + \nu}\right),$$

will satisfy these equations for any positive values of λ, μ, ν. Hence the surface over which the necessary equations are satisfied is the plane triangle formed by the three points $(\mathbf{M}v_1, \mathbf{M}S_1, \mathbf{M}E_1)$, $(\mathbf{M}v_2, \mathbf{M}S_2, \mathbf{M}E_2)$, $(\mathbf{M}v_3, \mathbf{M}S_3, \mathbf{M}E_3)$. The temperature and pressure all over this plane are the same and given by equations (169). Consequently any point within this triangle corresponds to a mixture of the three states of aggregation of a substance in equilibrium. This triangle is sometimes called the fundamental triangle, and represents the same conditions as the triple point on the $p - T$ diagram.

We are now in a position to state exactly what kind of equilibrium each point on the thermodynamic surface represents. If the point lies in either of the regions I, II, III, the substance will act as a homogeneous solid, liquid, or vapour respectively. If it lies in any of the regions (I II), (II III), or (III I), the system splits into two different states of aggregation indicated by the numerals used in this notation. The common temperature and pressure are completely determined by the inclination of the tangent plane to the planes $\mathbf{V} = 0$ and $\mathbf{S} = 0$, and the ratio of the masses of the two states is given by the ratio into which the point divides the line through this point connecting corresponding points on the boundary curves. Finally, if the point is within the fundamental triangle, the substance is a mixture of the three states, solid, liquid, and vapour, existing at the same temperature and pressure. The ratio of the masses of the various states can be obtained by solving equations (152), which give:

$$\mathbf{M}_1 : \mathbf{M}_2 : \mathbf{M}_3 : \mathbf{M} = \begin{vmatrix} \mathbf{M} & 1 & 1 \\ \mathbf{V} & v_2 & v_3 \\ \mathbf{E} & E_2 & E_3 \end{vmatrix} : \begin{vmatrix} \mathbf{M} & 1 & 1 \\ \mathbf{V} & v_3 & v_1 \\ \mathbf{E} & E_3 & E_1 \end{vmatrix} : \begin{vmatrix} \mathbf{M} & 1 & 1 \\ \mathbf{V} & v_1 & v_2 \\ \mathbf{E} & E_1 & E_2 \end{vmatrix} : \begin{vmatrix} \mathbf{M} & \mathbf{M} & \mathbf{M} \\ v_1 & v_2 & v_3 \\ E_1 & E_2 & E_3 \end{vmatrix}$$

CHAPTER IX

GASEOUS SYSTEMS AND THE NERNST HEAT THEOREM

81. The Perfect Gas Laws.—In the previous chapters various thermodynamic relations have been deduced for unit mass of any substance. Frequently it is of greater convenience to deal with one gram molecule, a mass equal to the molecular weight of the substance expressed in grams. This introduces certain simplifications, notably in the case of gases.

The characteristic equation for unit mass of a perfect gas is:

$$pv = RT,$$

where R is a constant for any one gas but varies from gas to gas. For one gram molecule the equation can be written in the form:

$$pv = MRT, . \qquad (173)$$

M being the molecular weight expressed in grams and v the volume occupied by one gram molecule.

For a different gas of molecular weight M_1 and gas constant R_1 we have

$$pv_1 = M_1R_1T. \qquad (174)$$

Comparing equations (173) and (174) for the same conditions of temperature and pressure it follows that

$$\frac{M_1R_1}{v_1} = \frac{MR}{v}.$$

The quantity $\frac{v}{M}$ is the volume of unit mass of the gas and is equal to $\frac{1}{Nm}$, where N is the number of molecules in unit volume and m is the mass of each molecule. Hence

$$N_1m_1R_1 = NmR.$$

Avogadro's hypothesis states that equal volumes of gases under the same conditions of temperature and pressure contain equal numbers of molecules. Therefore

$$N = N_1,$$

or

$$m_1 R_1 = mR.$$

But since

$$\frac{m_1}{m} = \frac{M_1}{M},$$

we have

$$M_1 R_1 = MR.$$

Thus, if we write

$$M_1 R_1 = MR = \boldsymbol{R},$$

the perfect gas equation for one gram molecule can be written:

$$pv = \boldsymbol{R}T, \quad \ldots \ldots \quad (175)$$

R being a universal constant, the same for all gases considered as perfect. The value of this constant is approximately 1·985 calories per degree C.

Equation (175) may be written in the form:

$$p = \frac{\boldsymbol{R}}{v} \,.\, T.$$

Now v is the volume occupied by one gram molecule of the gas, so that if ρ is the density of the gas we have:

$$v = \frac{M}{\rho},$$

and therefore

$$p = \frac{\rho}{M} \boldsymbol{R}T,$$

$$= \frac{N}{\boldsymbol{N}} \boldsymbol{R}T, \quad \ldots \ldots \quad (176)$$

where ***N*** is the number of molecules in one gram molecule and is the same for all substances. This universal constant is known as Avogadro's constant. If in equation (176) Boltzmann's constant

$\boldsymbol{k}$, the gas constant for one molecule, is substituted for $\dfrac{\boldsymbol{R}}{N}$, this reduces to

$$p = N\boldsymbol{k}T, \quad . \quad . \quad . \quad . \quad . \quad . \quad (177)$$

which gives the pressure exerted by any mass of gas in terms of the molecules contained in unit volume.

We have seen (Chapter VI) that the kinetic energy of the molecules in unit mass of gas is $\frac{3}{2}RT$. Consequently that of one gram molecule is $\frac{3}{2}\boldsymbol{R}T$, or $\frac{3}{2}\boldsymbol{k}T$ per molecule. This is equivalent to the statement that there is kinetic energy of amount $\frac{1}{2}\boldsymbol{k}T$ associated with each degree of freedom of the molecule.

Other relations which have been obtained in previous chapters can be expressed in terms of one gram molecule as easily as in terms of unit mass. For instance, the difference of the specific heats as given by the equation:

$$C_p - C_v = T\left(\frac{dp}{dT}\right)_v . \left(\frac{dv}{dT}\right)_p,$$

can be used to calculate the difference of the molecular heats, i.e. the quantities of heat necessary to raise the temperature of one gram molecule one degree at constant pressure and volume respectively, if the terms on the right-hand side of the equation are evaluated for the same mass. In this expression C_p and C_v are the *molecular* heats at constant pressure and volume respectively.

In the subsequent work all the results will be expressed per gram molecule and in terms of the universal gas constant $\boldsymbol{R}$.

82. Mixture of Gases.—It was found by Dalton that a mixture of gases contained in a vessel exerts a pressure on the walls equal to the sum of the pressures that would be exerted by the gases if they were present separately. This is known as *Dalton's Law of Partial Pressures*, and follows as a direct consequence of the elementary kinetic theory given in Chapter VI.

For a mixture of gases in which there are n_1 gram molecules of the first gas, n_2 of the second, n_3 of the third, and so on, the volume is given by:

$$\mathrm{v} = \frac{\boldsymbol{R}T}{p}(n_1 + n_2 + n_3 + \ldots),$$

$$= \frac{\boldsymbol{R}T}{p}\Sigma n_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (178)$$

The internal energy of a perfect gas is a function of the temperature only, and may be written:

$$E = \int^T C_v dT + e,$$

E being the internal energy per gram molecule, C_v the molecular heat at constant volume, and e a constant depending upon some arbitrarily fixed condition from which energy changes are measured. The integral cannot be evaluated unless the variation of C_v with temperature is known.

For a mixture of gases the expression for the total internal energy takes the form:

$$\mathbf{E} = \Sigma n_1 \left\{ \int^T (C_v) dT + e_1 \right\}, \quad . \quad . \quad . \quad . \quad (179)$$

where n_1, n_2, etc., are the gram molecules of the different gases present, the suffixes being used to distinguish the particular gas.

83. Entropy of a Mixture of Gases.—The entropy of one gram molecule of a perfect gas is given by equation (3~~7~~) is :(35).

$$S = \int^T \frac{C_p}{T} dT - \boldsymbol{R} \log p + C. \quad . \quad . \quad . \quad (180)$$

In order to calculate the entropy of a mixture of gases it is necessary to find some reversible means of separating them. This may be done in the following manner.

Let the gases be contained in a hollow cylinder as shown in Fig. 33. A and A′ are fixed walls, whilst B and B′ are coupled together and are movable in such a way that the distance BB′ remains fixed and equal to AA′. The walls B and A′ are supposed impermeable to either of the two gases forming the mixture, but A is permeable to the gas (1) and impermeable to (2), the reverse conditions holding for B′. At the commencement of the process B is in contact with A and B′ with A′, the intervening space containing the mixture of gases and that above B is supposed a vacuum. If the connected pistons B and B′ are slowly raised, the gas (1) will pass into the space between B and A, and the gas (2) into the space between A′ and B′. During this motion no external work will be done, as the total pressure on the coupled movable piston is zero. When B′ comes into contact with A the gases will be completely separated and no energy change can have taken place in the system if it is isolated so that it can neither gain nor lose heat. The temperature of each gas after the process will be the same as that of the mixture at the commencement; hence the total change of entropy is zero, as there has been no exchange of heat, and the process, if carried out infinitely slowly, is reversible.

From this it follows that the entropy of a mixture of gases is the same as the sum of the entropies which the two gases would have if at the same temperature each by itself occupied the whole volume of the mixture.

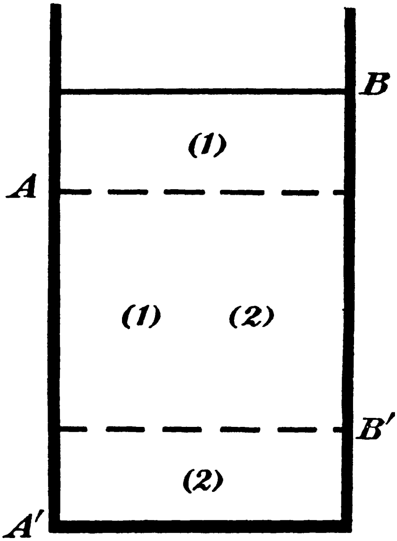

FIG. 33.

Using equation (180) we find, therefore, that the entropy of a mixture of perfect gases is given by:

$$\mathbf{S} = \Sigma n_1\left\{\int^T \frac{(C_p)_1}{T}dT - \mathbf{R}\log p_1 + C_1\right\}, \quad . \quad . \quad (181)$$

where $(C_p)_1$ is the molecular heat at constant pressure of the first gas, p_1 its partial pressure, and n_1 the gram molecules of this gas present.

By Dalton's law the pressure of the mixture is the sum of the partial pressures. That is:

$$p = \Sigma p_1.$$

Also the partial pressure of any gas in the mixture is proportional to the number of gram molecules present. Hence

$$p_1 : p_2 : p_3 : \ldots = n_1 : n_2 : n_3 : \ldots,$$

and therefore

$$p_1 = \frac{n_1}{n_1 + n_2 + n_3 + \ldots} \cdot p,$$

$$p_2 = \frac{n_2}{n_1 + n_2 + n_3 + \ldots} \cdot p, \text{ etc.}$$

Writing

$$c_1 = \frac{n_1}{\Sigma n_1},$$

$$c_2 = \frac{n_2}{\Sigma n_1}, \text{ etc.}$$

where $c_1, c_2, \ldots,$ are the concentrations, we obtain:

$$p_1 = c_1 p,\ p_2 = c_2 p,\ p_3 = c_3 p, \text{ etc.}$$

Using these relations, equation (181) for the entropy of the mixture becomes:

$$\mathbf{S} = \Sigma n_1 \left\{ \int^T \frac{(C_p)_1}{T} dT - \mathbf{R} \log c_1 p + C_1 \right\}$$

$$= \Sigma n_1 \left\{ \int^T \frac{(C_p)_1}{T} dT - \mathbf{R} \log p - \mathbf{R} \log c_1 + C_1 \right\}. \quad (182)$$

84. Change of Entropy in Diffusion.—We are now in a position to calculate the change of entropy when two gases diffuse into one another. Suppose we have two gases, n_1 and n_2 being the gram molecules of the first and second respectively. If they diffuse into one another at constant temperature and pressure, the same for the two gases, there is an increase in entropy of amount

$$-\mathbf{R}\{n_1 \log c_1 + n_2 \log c_2\}, \quad . \quad . \quad . \quad (183)$$

as the total entropy before diffusion is:

$$n_1 \left\{ \int^T \frac{(C_p)_1}{T} dT - \mathbf{R} \log p + C_1 \right\} + n_2 \left\{ \int^T \frac{(C_p)_2}{T} dT - \mathbf{R} \log p + C_2 \right\},$$

and after diffusion :

$$n_1\left\{\int^T \frac{(C_p)_1}{T}dT - \boldsymbol{R}\log c_1p + C_1\right\} + n_2\left\{\int^T \frac{(C_p)_2}{T}dT - \boldsymbol{R}\log c_2p + C_2\right\},$$

the difference as given by (183) being an essentially positive quantity as both c_1 and c_2 are fractions.

This is another example of the increase in entropy accompanying a natural irreversible process.

85. The Thermodynamic Potential.—For a mixture of gases the thermodynamic potential at constant pressure is defined by the equation:

$$\mathbf{G} = \mathbf{E} - T\mathbf{S} + p\mathbf{v}.$$

Substituting in this equation for $\mathbf{v}$, $\mathbf{E}$, and $\mathbf{S}$ from equations (178), (179), and (182), we have:

$$\mathbf{G} = \Sigma n_1\left\{\int^T (C_v)_1 dT + e_1 - T\int^T \frac{(C_p)_1}{T}dT + \boldsymbol{R}T\log c_1p - C_1T + \boldsymbol{R}T\right\}$$

But the thermodynamic potential of one gram molecule of the first gas at a temperature T and pressure p is given by:

$$G_1 = \int^T (C_v)_1 dT + e_1 - T\int^T \frac{(C_p)_1}{T}dT + \boldsymbol{R}T\log p - C_1T + \boldsymbol{R}T,$$

which by equation (21) reduces to :

$$G_1 = \int^T (C_p)_1 dT + e_1 - T\int^T \frac{(C_p)_1}{T}dT + \boldsymbol{R}T\log p - C_1T. \quad (184)$$

Hence

$$\mathbf{G} = \Sigma n_1\{G_1 + \boldsymbol{R}T\log c_1\}. \quad . \quad . \quad . \quad . \quad (185)$$

86. Equilibrium in Gaseous Systems at Constant Temperature and Pressure.—Suppose that in an imagined chemical change the numbers of gram molecules of the reactants n_1, n_2, . . . change by amounts dn_1, dn_2. . . . The corresponding change in $\mathbf{G}$ is given by

$$d\mathbf{G} = \Sigma\{G_1 + \boldsymbol{R}T\log c_1\}dn_1 + \Sigma n_1 d\{G_1 + \boldsymbol{R}T\log c_1\},$$

and for equilibrium at constant pressure and temperature this must be zero. That is, the condition for equilibrium in such a system is:

$$\Sigma\{G_1 + RT\log c_1\}dn_1 + \Sigma n_1 d\{G_1 + RT\log c_1\} = 0. \quad (186)$$

As $G_1, G_2, \ldots$ depend only upon the pressure and temperature, both of which are constant:

$$dG_1 = dG_2 = \ldots = 0.$$

Also

$$\begin{aligned} n_1 d\log c_1 + n_2 d\log c_2 + \ldots &= n_1\frac{dc_1}{c_1} + n_2\frac{dc_2}{c_2} + \ldots, \\ &= (n_1 + n_2 + \ldots)(dc_1 + dc_2 + \ldots), \\ &= 0, \end{aligned}$$

as by the definition of c_1, c_2, etc., their sum is unity.

Hence the condition of equilibrium (186) reduces to:

$$\Sigma\{G_1 + RT\log c_1\}dn_1 = 0. \quad . \quad . \quad . \quad (187)$$

This equation does not involve the absolute values of dn_1, $dn_2, \ldots$, but only their ratios, so we are able to put:

$$dn_1 : dn_2 : \ldots = \nu_1 : \nu_2 : \ldots \quad . \quad . \quad . \quad (188)$$

where $\nu_1, \nu_2, \ldots$ denote the numbers of gram molecules simultaneously passing into the mass of each constituent. Any one value of ν is positive if the substance to which it refers is formed during the reaction or change, and negative if the substance disappears. The numerical example below will make this clear.

Substituting from (188) in equation (187) the condition for equilibrium becomes:

$$\Sigma\nu_1\{G_1 + RT\log c_1\} = 0,$$

or

$$\nu_1\log c_1 + \nu_2\log c_2 + \ldots = -\frac{\nu_1 G_1 + \nu_2 G_2 + \ldots}{RT}.$$

The right-hand side of this equation depends only upon the pressure and temperature, and these are both constant. Hence we may write:

$$\Sigma\nu_1\log c_1 = \log K_c, \quad . \quad . \quad . \quad . \quad (189)$$

where for any given reaction K_c depends upon the pressure and temperature and is given by:

$$K_c = e^{-\Sigma \frac{\nu_1 G_1}{RT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (190)$$

The condition for equilibrium, equation (189), may be written in the alternative form:

$$c_1^{\nu_1} \, . \, c_2^{\nu_2} \, . \, c_3^{\nu_3} \, . \, . \, . = K_c \quad . \quad . \quad . \quad . \quad . \quad (191)$$

This is the *Law of Mass Action* and is of fundamental importance in the study of chemistry. K_c is called the reaction constant.

87. Numerical Example.—It has been pointed out that K_c is a constant for any given reaction depending upon the pressure and temperature alone. Consequently, if the value of K_c be found for a reaction when the reactants are mixed in known proportions, it is possible to calculate the final concentrations of the reacting substances if they are mixed in any known proportions and allowed to come to equilibrium under the same conditions of temperature and pressure.

The case of the dissociation of hydriodic acid has been very fully investigated by Bodenstein* and his co-workers, and provides a good example of the use of the mass-action law.

The equation for the reaction can be written:

$$H_2 + I_2 - 2HI = 0.$$

Supposing we start with hydriodic acid and raise it to such a temperature that it is partly dissociated. If the degree of dissociation be represented by x, there will be $(1 - x)$ gram molecules of HI and $\frac{x}{2}$ gram molecules of each of H_2 and I_2 (vapour) for each gram molecule of HI originally present. The concentration terms are, therefore:

Reactant	HI	H_2	I_2
c	$1 - x$	$\frac{x}{2}$	$\frac{x}{2}$.

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* Bodenstein, *Zeits. Phys. Chem.* **13**, 56 (1893); **22**, 1 (1897); **29**, 295 (1899).

Hence

$$K_c = c_1^{\nu_1} \cdot c_2^{\nu_2} \dots = \frac{\frac{x}{2} \times \frac{x}{2}}{(1 - x)^2} = \frac{x^2}{4(1 - x)^2}. \quad . \quad (192)$$

By starting with pure hydriodic acid and allowing equilibrium to be reached, and then analysing the mixture, the degree of dissociation x and hence K_c can be found.

Now consider the reverse reaction, starting from a mixture of H_2 and I_2. If there are originally q gram molecules of iodine and r gram molecules of hydrogen, and equilibrium is established when $2s$ gram molecules of HI are formed, the equilibrium constant is given by:

$$K_c = \frac{(q - s)(r - s)}{4s^2},$$

which solved for s gives:

$$s = \frac{q + r}{2(1 - 4K_c)} - \sqrt{\frac{(q + r)^2}{4(1 - 4K_c)^2} - \frac{qr}{(1 - 4K_c)}}. \quad (193)$$

Hence having found K_c from dissociation measurements and the use of equation (192), equation (193) gives a means of finding how much hydriodic acid will be formed at the same temperature and pressure when hydrogen and iodine are mixed in any known proportions.

The following table gives results found by Bodenstein. The value of x at a temperature of 357° C. was found to be 0·1946, and the calculated value of K_c from (192) 0·01494. Using this value, $2s$ could be calculated for a series of experiments in which hydrogen and iodine in different proportions formed the original mixture. In Table VI q, r, and s are given in ccs. (reduced

TABLE VI.

q.	r.	$2s$ Observed.	$2s$ Calculated.
2·59	6·63	4·98	5·02
5·71	6·22	9·55	9·60
10·40	6·41	11·88	11·68
26·22	6·41	12·54	12·34
23·81	6·21	12·17	11·98
22·29	6·51	12·71	12·68

to 0° C. and 760 mm.), as the number of gram molecules is proportional to the volume (Avogadro's hypothesis). The agreement between the last two columns is seen to be very satisfactory, especially when the experimental difficulties accompanying such work are borne in mind.

88. Alternative Expression for the Reaction Constant.—It is sometimes more convenient to have the reaction constant K_c expressed in terms of partial pressures rather than concentrations. If p is the total pressure of a mixture of gases, the partial pressures of which are p_1, p_2, etc., we have:

$$p_1 = c_1 p, \quad p_2 = c_2 p, \text{ etc.}$$

Substituting in equation (191) we obtain:

$$p_1^{\nu_1} \times p_2^{\nu_2} \times \ldots = p^{\nu_1 + \nu_2 + \cdots} \times K_c = K_p,$$

where K_p is the reaction constant in terms of pressure and is a true constant for constant temperature and pressure. Expressing the connection between K_c and K_p in the form:

$$K_p = p^{\Sigma \nu_1} \times K_c,$$

and taking logarithms of both sides, we have:

$$\log K_p = \Sigma \nu_1 \log p + \log K_c. \quad . \quad . \quad . \quad (194)$$

When there are solids and liquids present as well as the reacting gases the final state of equilibrium will be between the gases and the vapours of the solids and liquids. The vapour pressures of solids and liquids are functions of the temperature only, and therefore remain unaltered during the reaction. If the partial pressures of the substances present as solids or liquids be denoted by π with suitable subscripts, using p_1, p_2, . . . as before to refer to the gases, the equation for equilibrium becomes:

$$p_1^{\nu_1} \times p_2^{\nu_2} \times \ldots \pi_x^{\nu_x} \times \pi_y^{\nu_y} \times \ldots = K_p,$$

and as all the π's are constant this reduces to:

$$p_1^{\nu_1} \times p_2^{\nu_2} \times \ldots = K'_p.$$

Thus in applying the law of mass action to the equilibrium ot systems of which vapours form part it is only necessary to consider those reactants present as gases.

89. The Heat of Reaction.—We have already seen, equation (13), that when a substance is transformed from a state A to a state B the heat absorbed is given by:

$$\mathbf{q} = \mathbf{E}_B - \mathbf{E}_A + \mathbf{W},$$

where $\mathbf{q}$ and $\mathbf{W}$ are dependent upon the path adopted for the transformation. If external work can be done by means of volume changes only and the pressure is held constant this may be re-written as

$$\mathbf{q} = \mathbf{E}_B - \mathbf{E}_A + p\,(\mathbf{v}_B - \mathbf{v}_A).$$

By definition of the total heat the right-hand side of this equation is the difference of the total heats in the final and initial states, or:

$$\mathbf{q} = \mathbf{H}_B - \mathbf{H}_A.$$

When the substances taking part in the change are perfect gases we may, by the use of equations (178) and (179), write this in the form

$$\mathbf{H}_B - \mathbf{H}_A = \Sigma\nu_1 \left\{ \int^T (C_v)_1\, dT + e_1 + \mathbf{R}T \right\}. \quad . \quad (195)$$

The left-hand side of this equation is the heat absorbed in the change, i.e. the heat of reaction, and will be denoted by ΔH. Thus

$$\Delta H = \Sigma\nu_1 \left\{ \int^T (C_p)_1\, dT + e_1 \right\}, \quad . \quad . \quad . \quad (196)$$

since for a perfect gas the difference of the molecular heats is $\boldsymbol{R}$.

From equation (196) it is at once possible to find how the heat of reaction varies with temperature, for if ${}_{T_1}\Delta H$ is the heat of reaction at a temperature T_1 and ${}_{T_2}\Delta H$ that at T_2 we have:

$${}_{T_2}\Delta H - {}_{T_1}\Delta H = \Sigma\nu_1 \int_{T_1}^{T_2} (C_p)_1\, dT, \quad . \quad . \quad . \quad (196a)$$

and this difference can be calculated if the specific heats of the various reacting gases are known as functions of the temperature.

90. Effect of Changes of Pressure and Temperature on the Reaction Constant.—The effect of pressure on the reaction constant K_c can be found from equation (190). Taking logarithms of both sides of this equation it becomes:

$$\log K_c = -\frac{\Sigma\nu_1 G_1}{\boldsymbol{R}T} \quad . \quad . \quad . \quad . \quad . \quad (197)$$

Differentiating with respect to p, keeping T constant, we obtain:

$$\left(\frac{d \log K_c}{dp}\right)_T = -\frac{1}{RT}\Sigma\nu_1\left(\frac{dG_1}{dp}\right)_T,$$

which by use of equation (184) becomes:

$$\left(\frac{d \log K_c}{dp}\right)_T = -\frac{1}{RT}\Delta\mathbf{v}, \quad . \quad . \quad . \quad (198)$$

where $\Delta\mathbf{v}$ is the increase in volume when the reaction takes place, so that ν_1 gram molecules of the first substance, ν_2 of the second, and so on, are the amounts transformed.

Similarly by differentiating equation (197) with respect to T, keeping p constant, we have:

$$\left(\frac{d \log K_c}{dT}\right)_p = \frac{1}{RT^2}\Sigma\nu_1 G_1 - \frac{1}{RT}\left(\nu_1\frac{dG_1}{dT} + \nu_2\frac{dG_2}{dT} + \ldots\right),$$

and by substitution from equation (184):

$$\left(\frac{d \log K_c}{dT}\right)_p = \frac{1}{RT^2}\Sigma\nu_1\left\{\int^T (C_p)_1 dT + e_1\right\},$$

$$= \frac{\Delta H}{RT^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (199)$$

by the use of equation (196). This last equation is known as the *van't Hoff Isochore.*

Differentiating equation (194) with respect to T, keeping p constant, we obtain:

$$\left(\frac{d \log K_p}{dT}\right)_p = \left(\frac{d \log K_c}{dT}\right)_p = \frac{\Delta H}{RT^2}, \quad . \quad . \quad . \quad (200)$$

showing that at constant pressure K_p and K_c vary in the same manner with the temperature.

91. Principle of Le Chatelier.—From equation (199) and the definitions of K_c and ν it will be seen that if a reaction proceeds with an absorption of heat, i.e. ΔH is positive, when the temperature is raised the reaction has to proceed in a direction such that K_c is increased. That is, the reaction must go forward, forming new substances. In other words, an increase in the temperature causes the equilibrium to be displaced in the direction corresponding to absorption of heat from outside. The reverse conditions hold if ΔH is negative.

Equation (198) means that an increase of pressure results in a displacement of the equilibrium in the direction in which the reaction proceeds with diminution of volume.

These two statements are particular examples of a generalisation of wider applicability due to Le Chatelier. No "proof" in the ordinary sense can be given, but since its formulation the principle has been applied in many branches of physics and chemistry, and shown to be a valid and perfectly general law of nature. The principle may be stated as follows:

"If to a system in equilibrium a constraint be applied, a change takes place within the system tending to nullify the effect of the constraint and to restore equilibrium."

The same idea is conveyed by saying that every system in equilibrium is conservative and tends to remain unchanged. The principle can be illustrated by very simple examples.

If the pressure on a gas contained in a cylinder fitted with a piston is suddenly increased by pushing in the piston the volume is decreased; by the principle of Le Chatelier a change should take place in a direction such that this contraction will be partially annulled. Actually, of course, the gas is heated, and as gases expand on heating the change is in the direction required by the general principle.

In the case of a simple chemical reaction, such as dissociation, an increase in pressure lessens the dissociation if this normally occurs with increase of volume, for by the dissociation being lessened the volume, and therefore the pressure, is decreased.

Similarly, if the dissociation is accompanied by absorption of heat the change in the equilibrium produced by increasing the temperature will be to oppose the rise in temperature. That is, the degree of dissociation will be increased, for then heat will be absorbed, making the system tend to regain its original temperature.*

* See Rayleigh, *Journ. Chem. Soc.*, **111**, 250 (1917).

92. Numerical Example.—As an example of the use of the relations we have deduced we shall calculate the heat of dissociation of nitrogen tetroxide from equilibrium data.

Nitrogen tetroxide dissociates into nitrogen peroxide according to the equation :

$$N_2O_4 \rightleftarrows 2NO_2,$$

or

$$-N_2O_4 + 2NO_2 = 0.$$

Suppose p_1 to be the partial pressure of the nitrogen tetroxide, p_2 that of the peroxide, and p the total pressure. The reaction constant in terms of pressure is given by :

$$K_p = \frac{p_2^2}{p_1}. \qquad (201)$$

When equilibrium is established, suppose that the degree of dissociation is x, i.e. out of every gram molecule of nitrogen tetroxide originally present only a fraction $(1 - x)$ remains undissociated. As each molecule of nitrogen tetroxide forms two molecules of peroxide the ratio of the partial pressures is given by:

$$\frac{p_1}{p_2} = \frac{1 - x}{2x}. \qquad (202)$$

Also, since the sum of the partial pressures is equal to the total pressure :

$$p = p_1 + p_2. \qquad (203)$$

From equations (202) and (203) it follows that

$$p_1 = \frac{1 - x}{1 + x} \cdot p, \quad \text{and} \quad p_2 = \frac{2x}{1 + x} \cdot p,$$

whence from equation (201) :

$$K_p = \frac{4x^2}{1 - x^2} \cdot p. \qquad (204)$$

The ratio of the number of molecules present when equilibrium is established to the number which would have been present if no dissociation had taken place is :

$$(1 - x) + 2x : 1.$$

Consequently the densities of undissociated nitrogen tetroxide,

ρ_0, and of the partially dissociated mixture, ρ, must be in the ratio:

$$\frac{\rho_0}{\rho} = 1 + x,$$

or

$$x = \frac{\rho_0 - \rho}{\rho}. \quad . \quad . \quad . \quad . \quad . \quad (205)$$

Thus the degree of dissociation can be found directly by determinations of the densities or specific gravities of the undissociated nitrogen tetroxide and the partially dissociated mixture.

Substituting from (205) in equation (204) we have:

$$K_p = \frac{4(\rho_0 - \rho)^2}{\rho_0(2\rho - \rho_0)} \cdot p. \quad . \quad . \quad . \quad . \quad (206)$$

From experiment it is found that a mixture such as we are considering has the following specific gravities at the given temperatures referred to air as standard.

Temperature.	Specific Gravity.
26·7° C.	2·65
111·3° C.	1·65

The specific gravity of undissociated nitrogen tetroxide is 3·179. Substituting the above values for the specific gravities in equation (206) we find the values of K_p at 26·7° C. and 111·3° C. to be $0{\cdot}0415 \times 4p$ and $6{\cdot}08 \times 4p$ respectively.

By equation (200) the heat of reaction is given by:

$$\left(\frac{d \log K_p}{dT}\right)_p = \frac{\Delta H}{RT^2}.$$

This equation can be integrated if it is assumed that ΔH is constant over the range of temperature investigated. Thus:

$$\log \frac{(K_p)_1}{(K_p)_2} = \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right), \quad . \quad . \quad . \quad (207)$$

where $(K_p)_1$ is the reaction constant at temperature T_1 and $(K_p)_2$ that at T_2.

Substituting in equation (207) the values already obtained for $(K_p)_1$ and $(K_p)_2$ and $R = 1{\cdot}985$ calories, we obtain:

$$\Delta H = 13{,}480 \text{ calories.}$$

This is the amount of heat which is absorbed when one gram molecule of nitrogen tetroxide is completely dissociated at constant pressure. The observed value is about 13,200 calories, a very satisfactory agreement.

93. The Nernst Heat Theorem.—We have already had occasion to notice the occurrence of arbitrary constants in the equations deduced for the entropy of a substance; the first and second laws of thermodynamics give no means of determining these constants. The condition of equilibrium given by equation (190) cannot be completely determined until some means of finding the arbitrary constant is formulated.

By a theorem due to Nernst, however, the arbitrary constant can be completely eliminated and the conditions for equilibrium found without performing the reaction under consideration.

The theorem may be stated in a variety of ways, some of which are of greater implication than others. We shall follow that of Lewis and Gibson,* as, being the outcome of a consideration of a mass of theoretical and experimental data, it probably has the greatest claim to accuracy, and provides the most complete generalisation that our present knowledge allows.

"Every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of a perfect crystalline substance."

It will be seen that the entropy of any substance can now be calculated absolutely by starting with the substance at the absolute zero of temperature, and transforming it to the condition in which it is required to find the entropy by a reversible process, and evaluating the summation

$$\sum_0^T \frac{\delta q}{T}$$

for this path, the upper limit T being the temperature at which the entropy is required.

Planck† considers that any condensed chemically homogeneous substance, liquid or solid, has zero entropy at the absolute zero of temperature. Lewis and Gibson,* by a consideration of the connection between entropy and probability, came to the conclusion that this is not strictly true, the entropy of a liquid at the absolute zero being greater than that of the solid, the difference, however, being small.

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* Lewis and Randall, *Thermodynamics and the Free Energy of Chemical Substances*, p. 448.

† Planck, *Thermodynamics* (3rd Edition).

94. Illustrations of the Use of the Nernst Heat Theorem.—By means of the Nernst heat theorem a number of interesting conclusions in respect to certain properties of a body can be arrived at.

By the fourth thermodynamic relation we have:

$$\left(\frac{dS}{dp}\right)_T = -\left(\frac{dv}{dT}\right)_p.$$

For a crystalline solid the entropy at a temperature T is:

$$S = \int_0^T \frac{C_p^s}{T} dT, \quad . \quad . \quad . \quad . \quad . \quad . \quad (208)$$

the symbol C_p^s being used to denote the specific heat of a " condensed " system.

Hence

$$\left(\frac{dv}{dT}\right)_p = -\int_0^T \frac{1}{T} \cdot \frac{dC_p^s}{dp} . dT.$$

Using equation (54) for the variation of C_p^s with pressure this becomes:

$$\left(\frac{dv}{dT}\right)_p = \int_0^T \left(\frac{d^2v}{dT^2}\right)_p dT,$$

$$= \left[\left(\frac{dv}{dT}\right)_p\right]_0^T.$$

It follows, therefore, that $\left(\frac{dv}{dT}\right)_p$ is itself zero at the absolute zero of temperature. That is, the coefficient of expansion of a solid vanishes at the absolute zero. An empirical law of Grüneisen's, which states that the ratio of the coefficient of expansion to the specific heat is a constant, strengthens this conclusion, as it is well known that the specific heats of solids become very small in the neighbourhood of the absolute zero.*

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* Lewis and Gibson, *J.A.C.S.*, **39**, 2554 (1917), and **42**, 1529 (1920).

95. Temperature of Change of Phase.—For any change of phase the thermodynamic potential remains unchanged, i.e.:

$$G_1 = G_2,$$

the suffixes referring to the different phases.

Equation (208) gives the value of the entropy for any condensed system, so substituting in equation (160) we have:

$$H_1 - T\int_0^T \frac{(C_p^s)_1}{T} dT = H_2 - T\int_0^T \frac{(C_p^s)_2}{T} dT,$$

or

$$H_2 - H_1 = T\int_0^T \{(C_p^s)_2 - (C_p^s)_1\}\frac{dT}{T}.$$

For any change of state the difference of total heat in the two states is the latent heat. Hence, using the symbol L for the latent heat of one gram molecule,

$$L = T\int_0^T \{(C_p^s)_2 - (C_p^s)_1\}\frac{dT}{T}. \quad . \quad . \quad . \quad (209)$$

Now

$$C_p^s = \left(\frac{dH}{dT}\right)_p,$$

and therefore

$$(C_p^s)_2 - (C_p^s)_1 = \left(\frac{d(H_2 - H_1)}{dT}\right)_p = \frac{dL}{dT}.$$

Substituting in equation (209) we have, therefore,

$$L = T\int_0^T \frac{1}{T} \cdot \frac{dL}{dT} \cdot dT. \quad . \quad . \quad . \quad . \quad (210)$$

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* See Chapter XIII.

This equation may be used to calculate the melting-point or temperature of transformation of a substance if the latent heat is known as a function of the temperature.

Broensted* has found that the heat of transformation of rhombic into monoclinic sulphur is expressed by:

$$L = 1{\cdot}57 + 1{\cdot}15 \times 10^{-5} \, . \, T^2 \text{ calories.}$$

Substituting from this equation in equation (210) we obtain:

$$1{\cdot}57 + 1{\cdot}15 \times 10^{-5} \, . \, T^2 = 2{\cdot}30 \times 10^{-5} \, . \, T^2,$$

or

$$T = 369{\cdot}5^\circ.$$

Direct measurement gives the temperature as 368·4°, which is in as close agreement as could be expected.

96. Absolute Value of the Entropy of a Gas.—Making use of the Nernst heat theorem the entropy of a gas at a temperature T and pressure p can be calculated in a manner which involves no arbitrary constant and is therefore absolute.

Consider that the gas has been solidified and we have one gram molecule of the solid at the absolute zero; here its entropy is zero. Commencing with the solid at this temperature, let it be heated at constant pressure to a temperature T_1, below T, where the solid is completely vaporized, the latent heat being L and the vapour pressure p'. The vapour is next heated at constant pressure p' until the temperature T is reached, and then expanded to a pressure p. The entropy is given by:

$$S = \sum_0^T \frac{\delta q}{T} = \int_0^{T_1} \frac{C_p^s}{T} dT + \frac{L}{T_1} + \int_{T_1}^{T} \frac{C_p}{T} dT + \mathbf{R} \log \frac{p'}{p}.$$

Substituting in this equation the values of L and $\log p'$ given by equations (143) and (144), we obtain:

$$S = \frac{1}{T_1}\int_0^{T_1} C_p dT + \int_{T_1}^{T} \frac{C_p}{T} dT + \int_0^{T_1} \frac{dT}{T^2} \int_0^{T} C_p dT + \int_0^{T_1} \frac{C_p^s}{T} dT - \frac{1}{T_1}\int_0^{T_1} C_p^s dT$$

$$- \int_0^{T_1} \frac{dT}{T^2} \int_0^{T} C_p^s dT - \mathbf{R} \log p + \mathbf{R}i.$$

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* Broensted, *Zeit. Phys. Chem.*, **56**, 645 (1906).

Remembering that

$$\int_{T_1}^{T}\frac{C_p}{T}dT = \int_0^{T}\frac{C_p}{T}dT - \int_0^{T_1}\frac{C_p}{T}dT,$$

this equation becomes:

$$S = \int_0^{T}\frac{C_p}{T}dT - \boldsymbol{R}\log p + \boldsymbol{R}i$$

$$+\left\{\frac{1}{T_1}\int_0^{T_1}(C_p - C_p^s)dT - \int_0^{T_1}\frac{(C_p - C_p^s)}{T}dT + \int_0^{T_1}\frac{dT}{T^2}\int_0^{T}(C_p - C_p^s)dT\right\} \quad (211)$$

It is easily shown that the term in the bracket is zero, for it may be split into two terms of the form

$$\frac{1}{T_1}\int_0^{T_1} C_p dT - \int_0^{T_1}\frac{C_p}{T}\,dT + \int_0^{T_1}\frac{dT}{T^2}\int_0^{T} C_p\,dT.$$

Integrating the last term by parts it will be seen that the expression as a whole is zero. Equation (211) then reduces to the very simple form:

$$S = \int_0^{T}\frac{C_p}{T}dT - \boldsymbol{R}\log p + \boldsymbol{R}i. \quad . \quad . \quad . \quad (212)$$

97. The Equilibrium of Systems.—Equation (197) for the reaction constant contains two arbitrary constants, one involved in the internal energy and the other in the entropy. This may be seen by rewriting the equation in the form:

$$\begin{aligned}\boldsymbol{R}T\log K_c &= -\Sigma\nu_1 G_1,\\ &= -\Sigma\nu_1(E_1 - TS_1 + pv_1).\end{aligned}$$

By a determination of the heat of reaction one of these constants can be eliminated, for, writing the equation:

$$\boldsymbol{R}T\log K_c = -\Sigma\nu_1(E_1 + pv_1) + T\Sigma\nu_1 S_1,$$

we can, from equation (196), substitute ΔH for the first term on the right-hand side of this equation, which then becomes:

$$\boldsymbol{R}T \log K_c = -\Delta H + T\Sigma\nu_1 S_1 \quad . \quad . \quad . \quad (213)$$

Making use of Nernst's heat theorem we can substitute the value of S given by equation (212) in equation (213) and obtain:

$$\boldsymbol{R}T \log K_c = -\Delta H + T\Sigma\nu_1 \left\{ \int_0^T \frac{(C_p)_1}{T} dT - \boldsymbol{R} \log p + \boldsymbol{R} i_1 \right\},$$

or

$$\log K_c = \frac{-\Delta H}{\boldsymbol{R}T} + \frac{1}{\boldsymbol{R}} \Sigma\nu_1 \int_0^T \frac{(C_p)_1}{T} dT - \Sigma\nu_1 \log p + \Sigma\nu_1 i_1,$$

which by equation (194) reduces to:

$$\log K_p = \frac{-\Delta H}{\boldsymbol{R}T} + \frac{1}{\boldsymbol{R}} \cdot \Sigma\nu_1 \int_0^T \frac{(C_p)_1}{T} dT + \Sigma\nu_1 i_1. \quad . \quad (214)$$

Now, by equation (196*a*):

$$-\Delta H_0 = -\Delta H + \Sigma\nu_1 \int_0^T (C_p)_1 dT, \quad . \quad . \quad . \quad . \quad (215)$$

where ΔH and ΔH_0 are the heats of reaction at temperatures T and zero respectively. Substituting the value of ΔH given by (215) in equation (214) we have:

$$\log K_p = \frac{-\Delta H_0}{\boldsymbol{R}T} - \frac{1}{\boldsymbol{R}T} \cdot \Sigma\nu_1 \int_0^T (C_p)_1 dT + \frac{1}{\boldsymbol{R}} \Sigma\nu_1 \int_0^T \frac{(C_p)_1}{T} dT + \Sigma\nu_1 i_1. \quad (216)$$

But

$$\int_0^T \frac{C_p}{T} dT - \frac{1}{T} \int_0^T C_p dT = \int_0^T \frac{dT}{T^2} \int_0^T C_p dT,^*$$

and hence equation (216) becomes:

$$\log K_p = \frac{-\Delta H_0}{\boldsymbol{R}T} + \Sigma\nu_1 \int_0^T \frac{dT}{\boldsymbol{R}T^2} \int_0^T (C_p)_1 dT + \Sigma\nu_1 i_1. \quad . \quad (217)$$

---

* This may be verified by integrating by parts.

Further, from equation (200) we have:

$$\left(\frac{d\log K_p}{dT}\right)_p = \frac{\Delta H}{RT^2}.$$

Substituting in this equation the value of ΔH given by (215), and integrating, we obtain:

$$\log K_p = \frac{-\Delta H_0}{RT} + \Sigma\nu_1\int_0^T\frac{dT}{RT^2}\int_0^T(C_p)_1 dT + I, \quad . \quad (218)$$

where I is an integration constant.

Comparing equations (217) and (218) it is evident that if the Nernst heat theorem be true:

$$I = \Sigma\nu_1 i_1,$$

where i_1, i_2, . . . are the chemical constants of the reacting gases as determined from vapour pressure measurements. Hence according to this theorem a knowledge of the heat of reaction at one temperature, of the specific heats of the reacting gases and of the chemical constants of the gases, completely determines the equilibrium condition at any temperature.

In the foregoing only homogeneous reactions, i.e. reactions where the substances are all present in the gaseous phase, have been considered, but the method is easily extended to heterogeneous reactions, the result being of the form:

$$I = \Sigma\nu_1 i_1,$$

the summation sign in this case being taken to extend over the reactants which are present in the gaseous phase. The agreement between calculated and observed values of K_p is quite good, both for homogeneous and heterogeneous reactions.

98. The Dissociation of Water Vapour.—As an example of the use of the foregoing section we shall consider the dissociation of water vapour into hydrogen and oxygen.

The integration involved in equation (218) is in the general case difficult to perform, as the variation of C_p with temperature is not known as a rule over the range required, i.e. from the absolute zero to the temperature T. This difficulty can be avoided, however, by expanding ΔH in a power series of T, such as:

$$\Delta H = \Delta H_0 + \alpha T + \beta T^2 + \gamma T^3 + \ldots,$$

where the numerical coefficients $\Delta H_0, \alpha, \beta, \ldots$ must be determined by experiment. It has been shown by Nernst* that α can always be expressed in the form $3 \cdot 5 \, . \, \Sigma \nu_1$.

Substituting the above expression for ΔH in equation (200), and integrating, we have:

$$\log K_p = \frac{-\Delta H_0}{\boldsymbol{R}T} + \frac{\alpha}{\boldsymbol{R}} \log T + \frac{\beta T}{\boldsymbol{R}} + \frac{\gamma}{2\boldsymbol{R}} T^2 + \ldots + I.$$

But $I = \Sigma \nu_1 i_1$ if Nernst's heat theorem is true, so changing to logarithms to the base 10 and putting $\boldsymbol{R} = 1 \cdot 985$ calories this becomes:

$$\log_{10} K_p = \frac{-\Delta H_0}{4 \cdot 571 \, . \, T} + \Sigma \nu_1 \, 1 \cdot 75 \log_{10} T + \frac{\beta}{4 \cdot 571} \cdot T$$
$$+ \frac{\gamma}{2 \times 4 \cdot 571} \cdot T^2 + \ldots + \Sigma \nu_1 C_1, \quad . \quad (219)$$

where the above substitution has been made for α and $C_1, C_2, \ldots$ are the chemical constants when pressures are measured in atmospheres and logarithms expressed to the base 10.

Now consider the reaction:

$$-2H_2O + 2H_2 + O_2 = 0.$$

Suppose the degree of dissociation is x, which for this reaction is usually small in comparison with unity. Then the reaction constant at atmospheric pressure is given by:

$$K_p = \frac{x^3}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (220)$$

The experimental results for the heat of reaction for the dissociation of water can be expressed by the equation:

$$\Delta H = 113{,}880 + 3 \cdot 5T + 3 \cdot 5 \times 10^{-3} T^2$$
$$- 1 \cdot 33 \times 10^{-6} T^3 - 4 \times 10^{-10} T^4.$$

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* Nernst, *Theoretical Chemistry*, p. 756 (trans. 1916).

Substituting this value of ΔH in equation (219) we have:

$$\log_{10} K_p = -\frac{113{,}880}{4 \cdot 571\, T} + 1 \cdot 75 \log_{10} T + \frac{3 \cdot 5 \times 10^{-3}}{4 \cdot 571} T - \frac{6 \cdot 7 \times 10^{-7}}{4 \cdot 571} T^2 - \frac{1 \cdot 3 \times 10^{-10}}{4 \cdot 571} T^3 + \Sigma \nu_1 C_1. \quad . \quad (221)$$

Nernst gives the following values for the chemical constants:

Hydrogen = 1·6, Oxygen = 2·8, Water = 3·6.

Therefore

$$\Sigma \nu_1 C_1 = 2 \times 1 \cdot 6 + 2 \cdot 8 - 2 \times 3 \cdot 6 = -1 \cdot 2.$$

Making this substitution in equation (221) we have, finally:

$$\log_{10} K_p = -\frac{113{,}880}{4 \cdot 571\, T} + 1 \cdot 75 \log_{10} T + \frac{3 \cdot 5 \times 10^{-3}}{4 \cdot 571} T - \frac{6 \cdot 7 \times 10^{-7}}{4 \cdot 571} T^2 - \frac{1 \cdot 3 \times 10^{-10}}{4 \cdot 571} T^3 - 1 \cdot 2. \quad . \quad (222)$$

The following table gives the value of $\log_{10} K_p$ calculated from equations (220) and (222).

TABLE VII.

Absolute Temperature.	x.	$\log_{10} K_p$ (220).	$\log_{10} K_p$ (222).
1,300	$2 \cdot 7 \times 10^{-5}$	− 14·01	− 14·23
1,500	$1 \cdot 97 \times 10^{-4}$	− 11·42	− 11·54
1,561	$3 \cdot 4 \times 10^{-4}$	− 10·71	− 10·84
2,155	$1 \cdot 18 \times 10^{-2}$	− 6·09	− 6·25
2,300	$2 \cdot 6 \times 10^{-2}$	− 5·06	− 5·51

The agreement between the last two columns is fairly good. The small differences are, perhaps, due to the inadequacy of the thermal data, but the agreement is sufficient to establish the truth of the Nernst heat theorem, at any rate as a first approximation.

CHAPTER X

THE THERMODYNAMICS OF LIQUIDS AND DILUTE SOLUTIONS

99. Osmosis and Osmotic Pressure.—In the previous chapter we had occasion to imagine a semi-permeable membrane for the separation of a mixture of gases. There we were concerned exclusively with gases, but it has been known for a long time that a number of animal membranes are semi-permeable, allowing one substance to pass through them but retaining another. Nollet,* with an apparatus similar to that shown in Fig. 34, demonstrated that if an aqueous solution of sugar be placed in a tube which is closed at one end by an animal membrane and this dipped into water, the latter passes through the membrane into the solution, causing it to rise in the tube, but no sugar passes through into the pure solvent. This process of selective transmission through a membrane is termed *osmosis*. The pure solvent does not continue to pass into the solution indefinitely, but ceases when the hydrostatic pressure produced by the column of solution just counterbalances the force tending to cause water to diffuse through the membrane. This pressure is known as the *osmotic pressure* of the solution, and is the excess pressure which must be applied to a solution to bring it into equilibrium with the pure solvent. In the absence of a semi-permeable membrane the osmotic pressure results in the mixing of the solution and pure solvent by diffusion.

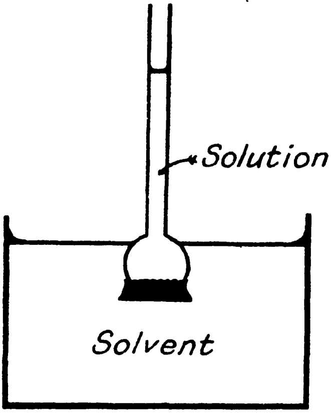

FIG. 34.

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* Nollet, *Recherches sur les causes de Bouillonnement des Liquides* (1748).

A few quantitative measurements of osmotic pressure were made by early experimenters using animal membranes, but reliable measurements were not forthcoming until Traube* discovered that artificial membranes of copper ferrocyanide could be used as semi-permeable membranes. Pfeffer† used such membranes deposited on the inner surface of porous clay cells, and the results he obtained were of much greater accuracy than those of previous workers in this field. Since Pfeffer's pioneer work a great deal of attention has been paid to the accurate measurement of osmotic pressure, and methods of very great accuracy have been developed by Morse and Frazer‡ in America, and Lord Berkeley and Hartley§ in England.

100. The Laws of Osmosis.—Although the actual mechanism by which osmosis takes place is not even yet fully understood, we are able to obtain the laws of osmosis for dilute solutions by the use of thermodynamics. The following proof is a modification of van't Hoff's || method of obtaining an expression for the osmotic pressure of a solution.

Consider a cylinder, such as shown in Fig. 35, containing a quantity of gas in equilibrium with a solution of the same gas. We shall regard the vapour pressure of the solvent as being negligible in comparison with the pressure of the gas. The solution is separated from the undissolved gas by the semi-permeable membrane *ab*, which allows the gas to pass through it but not the solvent. The walls *ac* and *bd* of the cylinder are in contact with pure solvent, to which they are permeable, but impermeable to the solute. The system being in equilibrium let us suppose that p is the pressure of the gas, v the volume of one gram molecule at this pressure, and P the osmotic pressure of the solution. Further, let us suppose that V is the volume of solution containing one gram molecule of solute; the molecular concentration of the solute, i.e. the gram molecules per unit volume, c, is then $\frac{1}{V}$. According to Henry's law the solubility of a gas is proportional

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* Traube, *Zentral. f. mediz. Wiss.* (1864), and *Archiv Anat. Wiss. Med.*, p. 87 (1867).

† Pfeffer, *Osmotische Untersuchungen* (1877).

‡ Morse, *Amer. Chem. Journ.* (1901–12).

§ Berkeley and Hartley, *Phil. Trans.*, A. **206**, 486 (1906).

|| van't Hoff, *Phil. Mag.*, **26**, 81 (1888).

to the pressure; that is, $c \propto p$. Suppose that the movable totally impermeable pistons which close the ends of the cylinder are both moved up so that one gram molecule of the dissolved gas is transferred from the liquid solution to the gaseous state. During this process the upper piston moves through a volume v, the reversible work done by the system being pv, whilst the lower piston moves through a volume V, the solvent passing out through the sides of the cylinder, and reversible work of amount PV being done on the system. The net work done by the system is $pv - PV$.

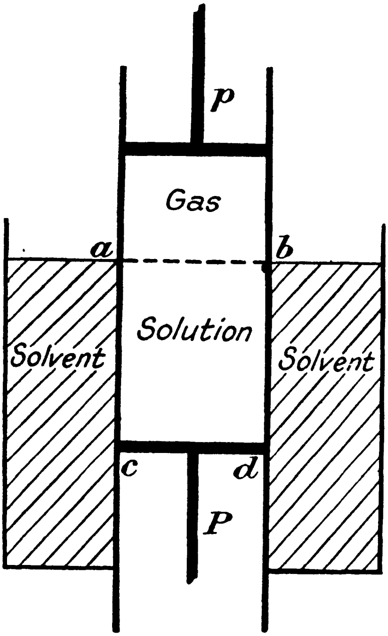

FIG. 35.

To complete an isothermal reversible cycle the gram molecule of gas forced out of the solution has to be restored to it by another isothermal reversible path. To do this imagine the gram molecule of gas of volume v and at pressure p to be isolated from the rest of the system by some means involving no work; for instance, by pushing across a weightless frictionless shutter. Let the volume so isolated be reversibly expanded to an extremely great volume v_∞. The work done by the system in this process is:

$$\int_{v}^{v_\infty} p\,dv = RT\int_{v}^{v_\infty}\frac{dv}{v} = RT\log\frac{v_\infty}{v}.$$

If the gas is now brought into contact with a volume V of solvent it will be absorbed infinitely slowly, as the dilution of the gas is practically infinite, and this process will, therefore, be reversible. If the gas is slowly compressed by lowering a piston it will eventually all dissolve in the volume V of solvent, the work done on the system in this process being:

$$\int_{0}^{v_\infty} p_1\,dv_1,$$

where p_1 is the pressure on the gas at any instant. The pressure on the gas being p_1, $(p_1 < p)$, the amount of gas which has gone into solution is $\frac{p_1}{p}$ gram molecules if Henry's law holds for the range of pressures we are considering, for when the pressure is p a volume V of solvent dissolves one gram molecule of gas. Consequently the mass of gas remaining undissolved is $\left(1 - \frac{p_1}{p}\right)$ gram molecules, and it is to this mass of gas that we must apply the gas equation. Hence, at any stage:

$$p_1 v_1 = \left(1 - \frac{p_1}{p}\right)RT = RT - p_1 v,$$

or

$$p_1 = \frac{RT}{v + v_1}.$$

Thus

$$\int_{0}^{v_\infty} p_1\,dv_1 = RT\int_{0}^{v_\infty}\frac{dv_1}{v + v_1} = RT\log\frac{v + v_\infty}{v}.$$

Neglecting v in comparison with v_∞ we obtain, as the work done on the system in dissolving one gram molecule of gas isothermally and reversibly in a volume V of solvent, the expression:

$$RT\log\frac{v_\infty}{v}$$

The gas has now been dissolved in the solvent, the solution being of the same concentration as that from which the gas was taken initially, and by adding this solution to that in the cylinder the whole system is restored to its initial condition. No work is involved in this last process, since the solutions are of the same concentration. A reversible isothermal cycle has now been completed, and the net amount of work done by the system must be zero. Hence

$$pv - PV + \boldsymbol{R}T \log \frac{v_\infty}{v} - \boldsymbol{R}T \log \frac{v_\infty}{v} = 0,$$

or

$$pv = PV.$$

But

$$pv = \boldsymbol{R}T,$$

and hence

$$PV = \boldsymbol{R}T, \quad \ldots \ldots \quad (223)$$

or expressed in terms of concentration:

$$P = c\boldsymbol{R}T. \quad \ldots \ldots \quad (224)$$

From equation (223) it will be seen that the osmotic pressure obeys the generalised gas law.

The proof given above refers only to osmotic pressure of gas solutions, and in the absence of a law for liquids and solids corresponding to Henry's law for gases the result cannot be rigidly extended to all solutions. There is ample experimental evidence, however, that the osmotic pressure of dilute solutions of substances which do not dissociate follow the gas laws. With electrolytic solutions the results, as would be expected, are more complicated, owing to the dissociation which accompanies solution in such cases. With very dilute solutions of binary electrolytes, in which dissociation is almost complete, the osmotic pressures are nearly double those given by equation (224), while very strong solutions approximate in effect more closely to the formula. This difference between electrolytic and non-conducting solutions is quite general, and applies in all the other results of osmosis.

101. The Vapour Pressure of a Solution.—It is found by experiment that the vapour pressure of a solution is less than that of the pure solvent. Applying the principle of Le Chatelier we can easily see that this must be so. First consider the pure solvent in equilibrium with its own vapour. If some non-volatile substance is now dissolved in it, the system, being conservative, tends to remain in its former state. This it accomplishes by condensing some of the vapour so as to lower the concentration of the solution, thereby making the vapour more dilute also, which is the same as lowering the vapour pressure.

By means of a reversible isothermal cycle the relation between the lowering of the vapour pressure and the concentration of the solution can be found.

Consider two vessels as shown in Fig. 36. In vessel 1 is pure solvent in contact with its own vapour at a pressure p_1, the system being in equilibrium. In vessel 2 there is a solution of a non-volatile substance in contact and equilibrium with its own vapour at the top, and at the bottom with pure solvent through a semi-permeable membrane; this membrane can be moved as a piston so as to transfer pure solvent from the solution. The two vessels are at the same temperature, and in each case the vapour is confined under a movable piston. The osmotic pressure of the solution will be denoted by P, and the vapour pressure by p, which is less than p_1.

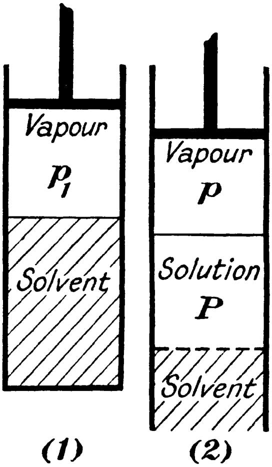

FIG. 36.

Let the following cycle now be performed. Evaporate a certain quantity of solvent, say *dn* gram molecules, from the first vessel and allow the vapour thus formed to expand isothermally and reversibly until its pressure falls to p, the same as the vapour pressure over the solution. Transfer the vapour to the vessel 2 and allow it to condense into the solution. The net work done by the substance in this process is:

$$p_1v_1 + \int_{p_1}^{p} pdv - pv,$$

where v_1 is the volume of the *dn* gram molecules of vapour under the pressure p_1, and v its volume under the pressure p. Integrating by parts this expression reduces to:

$$-\int_{p_1}^{p} vdp, \quad \text{or} \quad \int_{p}^{p_1} vdp.$$

Assuming the vapour behaves as a perfect gas this expression can be integrated, and we obtain as the work done:

$$dn\boldsymbol{R}T \log \frac{p_1}{p},$$

as only *dn* gram molecules have been transferred.

To restore the whole system to its initial state these *dn* gram molecules of solvent must be removed isothermally and reversibly from the solution and returned to the vessel 1. To do this move the lower piston of the vessel 2 until a volume *dV* of solvent corresponding to *dn* gram molecules has passed through the semi-permeable membrane. For the small change considered the osmotic pressure remains sensibly constant, and the work done on the system is *PdV*. The volume of solvent abstracted in this last process is then transferred to the vessel 1, and thus the initial state of the system is restored.

As all the processes have been made isothermally and reversibly the net work done in the cycle must be zero. Hence

$$dn\,\boldsymbol{R}T \log \frac{p_1}{p} - PdV = 0,$$

or

$$\log \frac{p_1}{p} = \frac{P}{\boldsymbol{R}T}\frac{dV}{dn}. \qquad (225)$$

Now the density of the liquid solvent, ρ, is given by:

$$\rho = M\frac{dn}{dV},$$

where M is the molecular weight. Hence, by substitution in equation (225), we have:

$$\log \frac{p_1}{p} = \frac{MP}{\rho \boldsymbol{R}T}, \qquad (226)$$

which by equation (224) becomes:

$$\log \frac{p_1}{p} = \frac{cM}{\rho}.$$

If p and p_1 differ by only a small amount the logarithmic term may be expanded and the equation becomes:

$$\frac{p_1 - p}{p} = \frac{cM}{\rho}.$$

This result assumes a simpler form if expressed in terms of gram molecules of solute and solvent respectively. Suppose we have a mass of solute corresponding to n gram molecules dissolved in a volume $\mathbf{V}$ of solvent. Then by definition:

TABLE VIII.

$\frac{n}{N+n}$	$\frac{p_1 - p}{p_1}$	$\frac{n}{N+n}$	$\frac{p_1 - p}{p_1}$
0° C.:—		30° C.:—	
0·00359	0·00372	0·0177	0·0194
0·00893	0·00945	0·0297	0·0349
0·0177	0·0197	100° C.:—	
20–25° C.:—		0·00538	0·00546
0·00179	0·00176	0·0107	0·0111
0·00716	0·00720	0·0142	0·0150
0·0177	0·0191		

$$c = \frac{n}{\mathbf{V}}.$$

Substituting this value of c in the previous equation we have:

$$\frac{p_1 - p}{p} = \frac{nM}{\rho \mathbf{V}},$$
$$= \frac{n}{N}$$

where N is the number of gram molecules of solvent in the volume $\mathbf{V}$. This equation may be rewritten as;

$$\frac{p_1 - p}{p_1} = \frac{n}{N + n}. \quad . \quad . \quad . \quad . \quad . \quad (226a)$$

The fraction $\frac{p_1 - p}{p_1}$ is the proportional or relative lowering of the vapour pressure; this is independent of the temperature.

Table VIII, page 179, shows the degree of agreement between the calculated and observed values of the relative lowering of vapour pressure for a solution of sucrose ($C_{12}H_{22}O_{11}$) in water.*

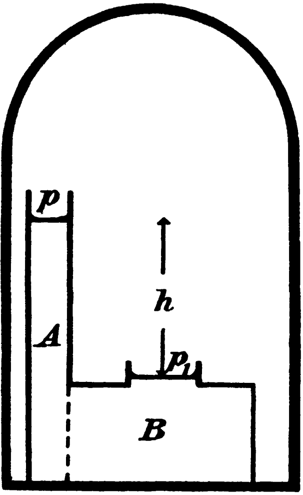

FIG. 37.

102. Alternative Method for the Vapour Pressure of a Solution.

—The equation for the vapour pressure of a solution can be deduced without the aid of thermodynamics.

Consider an enclosure, Fig. 37, which contains a vessel divided into two portions A and B by a semi-permeable membrane. In the portion B is pure solvent and in A a solution of some non-volatile substance in the same solvent. There will be a difference of level between the surfaces of the solvent and solution, the hydrostatic pressure exerted by the column of solution just balancing the osmotic pressure when equilibrium is attained.

Let the vapour pressures just above the surfaces be p_1 and p as shown, and the difference of level h. If ρ is the density of the solution, considered the same as that of the pure solvent as the concentrations with which we are dealing are small, we have:

$$P = \rho g h, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (227)$$

P being the osmotic pressure, and g the acceleration due to gravity.

Also for the change in pressure of the vapour with height we have:

$$dp = -\sigma g dh,$$

---

* International Critical Constants, 3, 293.

where σ is the density of the vapour. Now this is given by:

$$\sigma = \frac{Mp}{RT},$$

if the vapour be regarded as a perfect gas, M being the molecular weight. Substituting this value of σ in the previous equation we have:

$$\frac{dp}{p} = -\frac{M}{RT} \cdot gdh,$$

which on integration becomes:

$$\log \frac{p_1}{p} = \frac{Mgh}{RT},$$

and substituting for gh from equation (227):

$$\log \frac{p_1}{p} = \frac{MP}{\rho RT}.$$

This is the same expression as we deduced previously.

103. Elevation of the Boiling-Point.—A liquid boils when its vapour pressure is equal to the external pressure. We have seen that a non-volatile substance dissolved in a liquid lowers the vapour pressure, so that the temperature at which a solution boils is higher than the boiling-point of the pure solvent. This elevation of the boiling-point may be evaluated as follows: Fig. 38 represents two enclosures, the vessel 1 containing a solution in equilibrium with the vapour of the pure solvent at a temperature $T + \Delta T$, where the vapour pressure of the solution is equal to the external pressure. The solution is confined by a semi-permeable membrane which can be moved as a piston. Vessel 2 contains pure solvent in equilibrium with its vapour at a temperature T, the boiling-point of the solvent. In each case the vapour is confined under a movable piston. Let the following cycle now be performed.

(i) In the vessel 1 vaporize dm grams of the solvent. If we denote the latent heat of vaporization per gram at the temperature $T + \Delta T$ by $l + \Delta l$ the heat absorbed is $(l + \Delta l)\, dm$, and reversible work of amount pdv is done by the system.

(ii) Let this vapour be cooled to the temperature T and transferred to the vessel 2. The heat given out in this process is $k_1 dm\Delta T$, where k_1 is the specific heat of the vapour.

(iii) The vapour is now condensed in the vessel 2, giving out heat ldm and having work of amount pdv (approximately) done on it. Let the volume of liquid formed be dV.

(iv) This volume, dV, of liquid is now isolated from the liquid in the vessel 2, its temperature raised to $T + \Delta T$, and then reversibly returned to the vessel 1 by the semi-permeable membrane. The heat absorbed in this process is $k_2 dm\Delta T$, and the work done by the system PdV, k_2 being the specific heat of the liquid and P the osmotic pressure of the solution. This completes the cycle.

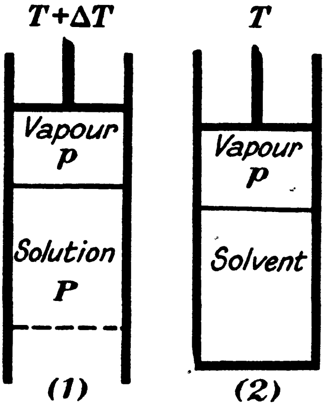

FIG. 38.

The working substance having performed a reversible cycle of operations and returned to its initial conditions, the external work done must be equal to the net heat absorbed, and the total change of entropy be zero. Hence equating heat absorbed to external work done we have:

$$(l + \Delta l)dm - k_1 dm\Delta T - ldm + k_2 dm\Delta T = PdV,$$

and for the change of entropy:

$$\frac{l + \Delta l}{T + \Delta T} - \frac{k_1\Delta T}{T} - \frac{l}{T} + \frac{k_2\Delta T}{T} = 0.$$

These equations reduce to:

$$\Delta l - (k_1 - k_2)\Delta T = P\frac{dV}{dm},$$

and

$$\Delta l - l\frac{\Delta T}{T} - (k_1 - k_2)\Delta T = 0,$$

respectively, neglecting the products of small quantities.

Hence by subtraction we have:

$$l\frac{\Delta T}{T} = P\frac{dV}{dm}. \quad \ldots \ldots \quad (228)$$

But $\frac{dm}{dV} = \rho$, the density of the solvent, and $P = c\boldsymbol{R}T$. Making these substitutions in equation (228) this becomes:

$$\Delta T = \frac{c\boldsymbol{R}T^2}{l\rho}, \quad \ldots \ldots \quad (229)$$

which is the thermodynamically accurate form for the relation between rise of boiling-point and concentration.

104. Depression of the Freezing-Point.—In the same way as the presence of a non-volatile solute raises the boiling-point of a solution so does it lower the freezing-point. A familiar example of this effect is a mixture of ice and saturated salt solution which has a fixed temperature considerably below the ice point, and is used for the zero on the Fahrenheit scale of temperature. By a similar cycle to that used in the previous section we can deduce the magnitude of the effect.

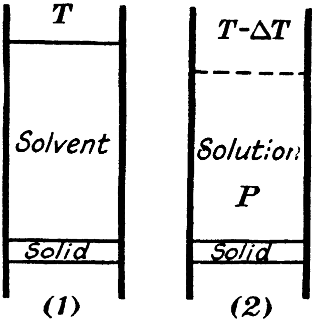

FIG. 39.

In Fig. 39 are shown two vessels, the first containing pure solvent in contact with frozen solvent at the temperature T, and the second containing solution in contact with frozen solvent at the temperature $T - \Delta T$. At the top of vessel 2 is a semi-permeable membrane to allow of the reversible transfer of pure solvent to the solution. Let the following cycle now be performed.

(i) Melt dm grams of the solid in vessel 1 to form a volume dV of solvent. In this process heat of amount ldm will be absorbed, and a small amount of work done by the system which will cancel with that in (iii).

(ii) Cool the liquid formed in the first process to the temperature $T - \Delta T$ and then reversibly transfer it to the solution in vessel 2 by the semi-permeable membrane. The heat given out and the work done by the system in this process are $k_1 dm\Delta T$ and PdV respectively if k_1 is the specific heat of the liquid and P the osmotic pressure of the solution.

(iii) Let the dm grams of solvent be condensed to the solid at the temperature $T - \Delta T$, giving out heat $(l - \Delta l)dm$, where $(l - \Delta l)$ is the latent heat of fusion per gram at this temperature, and having a small amount of work done on it.

(iv) The mass of solid of the temperature $T - \Delta T$ is now transferred from the vessel 2 to the vessel 1, absorbing heat $k_{12}dm\Delta T$ if k_2 is the specific heat of the solid.

As before, equating the external work done to the heat absorbed and the change of entropy to zero, we have:

$$ldm - k_1 dm\Delta T - (l - \Delta l)dm + k_2 dm\Delta T = PdV,$$

and

$$\frac{l}{T} - \frac{k_1\Delta T}{T} - \frac{l - \Delta l}{T - \Delta T} + \frac{k_2\Delta T}{T} = 0,$$

which reduce to:

$$\Delta l - (k_1 - k_2)\Delta T = P\frac{dV}{dm},$$

and

$$\Delta l - l\frac{\Delta T}{T} - (k_1 - k_2)\Delta T = 0,$$

respectively.

Hence by subtraction we have:

$$l\frac{\Delta T}{T} = P\frac{dV}{dm},$$

and substituting $\frac{dm}{dV} = \rho$, and $P = cRT$, this becomes:

$$\Delta T = \frac{cRT^2}{l\rho}. \qquad \ldots\ldots \qquad (230)$$

This equation for the depression of the freezing-point is of the same form as that obtained for the elevation of the boiling-point. It must be noticed, however, that ΔT is positive in the case of the effect on the boiling-point, but negative for the effect on the freezing-point.

105. The Thermodynamic Potential of a Solution.—The equation for the depression of the freezing-point can be deduced from the thermodynamic potential at constant pressure in the following manner.

Suppose we have n_1 gram molecules of solvent, and in it are dissolved n_2 gram molecules of some non-volatile solute, n_3 of another, and so on.

The total volume occupied by the solution is given by:

$$\mathbf{v} = n_1 v_1 + n_2 v_2 + n_3 v_3 + \ldots,$$

where v_2, v_3, etc., depend upon the solvent as well as the solute, but are not influenced by the mutual interaction of the solutes or of the molecules of a given solute amongst themselves.

The internal energy of the whole system is given by:

$$\mathbf{E} = n_1 E_1 + n_2 E_2 + n_3 E_3 + \ldots$$

For the entropy we have:

$$d\mathbf{S} = \frac{d\mathbf{E} + p\,d\mathbf{v}}{T} = n_1 \cdot \frac{dE_1 + p\,dv_1}{T} + n_2 \cdot \frac{dE_2 + p\,dv_2}{T} + \ldots,$$

and since $E_1, E_2, \ldots$ and $v_1, v_2, \ldots$ are independent of $n_1, n_2, \ldots$, and only dependent upon p and T, we can write:

$$d\mathbf{S} = n_1 dS_1 + n_2\, dS_2 + n_3 dS_3 + \ldots$$

Integrating this equation we have:

$$\mathbf{S} = n_1 S_1 + n_2 S_2 + n_3 S_3 + \ldots + C,$$

where C is an integration constant.

Hence

$$\begin{aligned} \mathbf{G} &= \mathbf{E} - T\mathbf{S} + p\mathbf{v}, \\ &= \Sigma n_1(E_1 + pv_1 - TS_1) + C, \\ &= \Sigma n_1 G_1 + C. \qquad (231) \end{aligned}$$

By its nature the integration constant C is independent of p and T, but it may depend upon $n_1, n_2, \ldots$. Planck uses the following device to obtain its value.

Imagine the temperature to be increased and the pressure decreased until the whole system behaves as a perfect gas. The thermodynamic potential of a mixture of perfect gases is given by equation (185) as:

$$\mathbf{G} = \Sigma n_1 \{G_1 + RT \log c_1\}.$$

Comparing this with equation (231) we see that

$$C = \Sigma n_1 \boldsymbol{R}T \log c_1,$$

and therefore the thermodynamic potential of a solution is given by:

$$\mathbf{G} = \Sigma n_1\{G_1 + \boldsymbol{R}T \log c_1\}.$$

To find the depression of the freezing-point suppose we have n_2 gram molecules of solute dissolved in n_1 gram molecules of solvent. Then

$$c_1 = \frac{n_1}{n_1 + n_2}, \quad c_2 = \frac{n_2}{n_1 + n_2},$$

and the thermodynamic potential of the solution is given by:

$$\mathbf{G} = n_1\{G_1 + \boldsymbol{R}T \log c_1\} + n_2\{G_2 + \boldsymbol{R}T \log c_2\}.$$

If the solution be at its freezing-point the pure solvent can separate out reversibly. Let dn_1 gram molecules of the solvent leave the solution and enter the solid state. This change takes place at constant temperature and pressure, so the total change in thermodynamic potential is zero. The decrease in the thermodynamic potential of the solution by the departure of dn_1 gram molecules of solvent is $dn_1\{G_1 + \boldsymbol{R}T \log c_1\}$; but the thermodynamic potential of the solid increases by $G_1'dn_2$ on gaining dn_1 gram molecules if G_1' is the thermodynamic potential of one gram molecule of the solid. Hence we have:

$$dn_1\{G_1 + \boldsymbol{R}T \log c_1\} - G_1'dn_1 = 0,$$

or

$$G_1 - G_1' = -\boldsymbol{R}T \log c_1.$$

If we are dealing with pure solvent $c_1 = 1$, and we have, as before, the equality of the thermodynamic potential of the solid and liquid states when in equilibrium with one another.

Let us suppose that the freezing-point of the solution is ΔT lower than that of the pure solvent. Then ΔT is the amount by which the temperature must be changed to bring $G_1 - G_1'$ from the value zero to the value $-\boldsymbol{R}T \log c_1$. That is:

$$\Delta T \frac{d}{dT}(G_1 - G_1') = \boldsymbol{R}T \log c_1,$$

or, since

$$\left(\frac{dG}{dT}\right)_p = -S,$$

$$\Delta T (S_1' - S_1) = RT \log c_1. \quad . \quad . \quad . \quad (232)$$

But in any change of state:

$$S_1 - S_1' = \frac{Ml}{T},$$

where l is the latent heat per gram and M the molecular weight of the solvent. Substituting in equation (232), we have:

$$\Delta T \frac{Ml}{T} = -RT \log c_1.$$

But

$$c_1 = 1 - c_2,$$

and therefore

$$\Delta T \frac{Ml}{T} = -RT \log (1 - c_2).$$

As c_2 is small, as we are considering dilute solutions, the logarithmic term may be expanded as:

$$\log (1 - c_2) = -c_2,$$

and

$$\Delta T = \frac{c_2 RT^2}{Ml}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (233)$$

Since

$$c_2 = \frac{n_1}{n_1 + n_2},$$

and n_1 is small in comparison with n_2, we can write:

$$c_2 = \frac{n_1}{n_2}.$$

Now

$$c = \frac{n_1}{V},$$

and multiplying top and bottom by $\frac{\rho}{M}$ we obtain:

$$c = \frac{n_1}{n_2} \cdot \frac{\rho}{M},$$

or

$$c_2 = c \cdot \frac{M}{\rho},$$

where ρ is the density of the solvent. Substituting this value of c_2 in equation (233) this becomes:

$$\Delta T = \frac{cRT^2}{l\rho},$$

the familiar result.

106. Determination of Molecular Weights.—The elevation of the boiling-point and the depression of the freezing-point both serve as methods for the determination of molecular weights. Let us consider the elevation of boiling-point produced by dissolving one gram molecule of a substance in 100 grams of solvent. In this case

$$c = \frac{1}{100} \cdot \rho,$$

and therefore

$$\Delta T = \frac{RT^2}{100\,l} = D. \qquad (234)$$

This quantity is a constant for a particular solvent and is known as the molecular rise of boiling-point. Similarly, in the case of the freezing-point the depression produced by dissolving one gram molecule of solute in 100 grams of solvent is called the molecular lowering of freezing-point. The following table, taken from Raoult's experimental data, illustrates the constancy of the molecular depression for very different solutes.

TABLE IX.

Solutions in Benzene.		Solutions in Water.	
Solute.	Molecular Depression.	Solute.	Molecular Depression.
Methyl iodide ..	50·4	Urea	17·2
Nitrobenzene ..	48·0	Ethyl acetate ..	17·8
Naphthalene ..	50·0	Acetic acid	19·0
Anthracene	51·2	Cane sugar	18·5

If we have a mass of solute m, dissolved in a mass W of solvent, the elevation of boiling-point produced will be:

$$\Delta T = \frac{m}{M'W}\frac{RT^2}{l},$$

$$= \frac{100\,m}{M'W}\,D, \quad . \quad . \quad . \quad . \quad . \quad . \quad (235)$$

where M' is the molecular weight of the dissolved substance and D the molecular elevation for the particular solvent. This equation can be used to determine M'.

As an example we shall consider the following problem.

"An elevation of the boiling-point of 1·09° C is produced by dissolving 0·674 gram of camphor in 6·81 grams of acetone. What is the molecular weight of camphor?"

From tables we obtain the following data:

Boiling-point of acetone = 56·1° C.
Latent heat of vaporization = 124·5 calories per gm.
R = 1·985 calories per ° C.

Hence the molecular elevation, D, is given by:

$$D = \frac{1{\cdot}985 \times (329{\cdot}2)^2}{100 \times 124{\cdot}5},$$

$$= 17{\cdot}3^\circ\ \mathrm{C}.$$

Substituting this value of D in equation (235), and the appropriate values for m, W, and ΔT, we obtain:

$$M' = \frac{100 \times 0{\cdot}674 \times 17{\cdot}3}{6{\cdot}81 \times 1{\cdot}09}.$$

$$= 157.$$

The formula for camphor, $C_{10}H_{16}O$, requires a value of 152 for the molecular weight. Hence the molecular weight of camphor in acetone solution is in accordance with the simplest formula that expresses its composition.

The methods of elevation of boiling-point and depression of freezing-point are of wide application in chemistry for the determination of molecular weights. For experimental details and limits imposed upon the methods by certain solutes, e.g. electrolytes, the student is referred to textbooks of physical chemistry.

107. Osmotic Pressure Formulæ for Higher Concentrations.—The simple form of equation for the osmotic pressure of a solution:

$$P = c\boldsymbol{R}T,$$

is applicable to dilute solutions, but experiment shows that it fails for higher concentrations. From equation (226) we can deduce an equation for the osmotic pressure which represents the experimental results for varying concentrations with greater accuracy. We have:

$$\log \frac{p_1}{p} = \frac{MP}{\rho \boldsymbol{R}T}.$$

Substituting V_0, the volume occupied by one gram molecule of solvent, for $\frac{M}{\rho}$ in this equation and rearranging, it becomes:

$$P = \frac{\boldsymbol{R}T}{V_0}\left[-\log \frac{p}{p_1}\right], \quad . \quad . \quad . \quad . \quad (236)$$

which is the exact equation for all concentrations, provided the perfect gas laws apply to the vapour and the effect of pressure on V_0 is negligible.

From equation (226*a*) we have:

$$\begin{aligned}\frac{p}{p_1} &= 1 - \frac{n}{N+n},\\ &= 1 - x,\end{aligned}$$

where x is written for $\frac{n}{N+n}$. Substituting this value of the ratio $\frac{p}{p_1}$ in equation (236), this becomes:

$$P = \frac{\boldsymbol{R}T}{V_0}[-\log(1 - x)],$$

or expanding the logarithmic term:

$$P = \frac{\boldsymbol{R}T}{V_0}(x + \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 + \ldots). \quad . \quad . \quad (237)$$

There is considerable experimental evidence that when sugar is dissolved in water hydrates are formed. Let us suppose that each molecule of sugar combines, on the average, with β molecules of solvent. If the number of gram molecules of sugar in 1,000 grams of water is y, we have:

$$x = \frac{y}{55{\cdot}5 + y - \beta y}$$

instead of

$$x = \frac{y}{55{\cdot}5 + y},$$

which would be the value if no hydration of the solute took place, 55·5 being the gram molecules of water in 1,000 grams.

The following table gives the observed values of the osmotic pressure of cane-sugar solutions in atmospheres at 20° C., and the values as calculated from equation (237),* first assuming no hydration, and secondly assuming $\beta = 5$, and that this remains constant throughout the range of concentration studied.

TABLE X.

Gram Molecules of Sugar per 1,000 Grams of Water.	Osmotic Pressure Observed.	Osmotic Pressure. Calculated by Equation (237).	
		Assuming no Hydration.	Assuming Hydration $= 5H_2O$.
0·1	2·59	2·38	2·41
0·2	5·06	4·76	4·85
0·3	7·61	7·14	7·33
0·4	10·14	9·51	9·87
0·5	12·75	11·87	12·43
0·6	15·39	14·24	15·05
0·7	18·13	16·59	17·71
0·8	20·91	18·94	20·42
0·9	23·72	21·29	23·15
1·0	26·64	23·64	25·96

108. Vapour Pressure over a Curved Surface.—It was demonstrated by Lord Kelvin† that the vapour pressure of a liquid with a curved surface must be different from that of the same liquid with a plane surface. Suppose we have a closed vessel (Fig. 40) which contains the liquid and its vapour only, and that a narrow capillary tube of radius r is placed in the liquid. The liquid will rise in this tube to a height h above the level of the liquid outside the tube. Let p be the saturation vapour pressure just above the plane surface, and p_1 that above the curved surface

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* Only the first two terms in brackets used for purposes of calculation.

† *Proc R.S.E.* (1870).

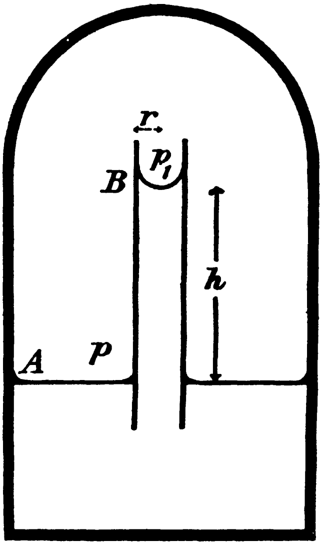

FIG. 40.

of radius r at B. The difference between these two pressures is due to the pressure of the column of vapour of height h. Thus:

$$p - p_1 = g\sigma h \quad . \quad . \quad . \quad . \quad . \quad . \quad (238)$$

where σ is the vapour density. The pressure at A is p, while that just below the meniscus in the liquid at B is $p - g\rho h$, and, since there is an excess pressure inside the curved surface of $\frac{2\gamma}{r}$, ρ being the density of the liquid and γ the surface tension, we have:

$$p_1 = p - g\rho h + \frac{2\gamma}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (239)$$

Eliminating gh between equations (238) and (239) we obtain:

$$p - p_1 = \frac{2\gamma}{r} \cdot \frac{\sigma}{\rho - \sigma}.$$

Lord Kelvin* regarded this effect as being due to curvature, but Poynting† showed that it might be regarded simply as an effect of hydrostatic pressure. That is, if the difference of hydrostatic pressures under the curved and plane surfaces be denoted by P, we have:

$$P = g\rho h,$$

and hence, from equation (238) and our previous result:

$$p - p_1 = P \cdot \frac{\sigma}{\rho} = \frac{2\gamma}{r} \cdot \frac{\sigma}{\rho - \sigma}. \quad . \quad . \quad . \quad (240)$$

If the height h is large the above expression for the difference of vapour pressure is not sufficiently accurate, as the variation of vapour pressure with height has not been taken into account. For any small change when the vapour pressure changes by dp and the hydrostatic pressure by dP we have:

$$\frac{dp}{\sigma} = \frac{dP}{\rho},$$

or

$$vdp = Vdp,$$

where v and V are the specific volumes of the vapour and liquid respectively. To obtain the variation of vapour pressure with hydrostatic pressure this equation must be integrated between the corresponding values of p and P. That is:

$$\int_{p_1}^{p} vdp = \int_{0}^{P} VdP.$$

Assuming the vapour obeys the perfect gas laws and that the compressibility of the liquid is negligible, this becomes:

$$RT\int^{p} \frac{dp}{p_1} = PV,$$

---

* Kelvin, *Phil. Mag.*, **42**, 448 (1871).

† Poynting, *Phil. Mag.*, 40 (1881).

or

$$RT \,.\log \frac{p}{p_1} = \frac{P}{\rho},$$

where P is the pressure to be applied to the liquid in order to change the vapour pressure from p_1 to p.

C. T. R. Wilson* has observed that in the absence of nuclei a very fine mist is formed in water vapour on sudden expansion when its density is about eight times the saturation value. Putting $\frac{p}{p_1} = 8$, and taking for water $R = 4{\cdot}61 \times 10^6$ and the temperature at 300° K, we find $P = 2{,}800$ atmospheres approximately. Taking $P = 2{,}800$ atmospheres and assuming the formula $\frac{2\gamma}{r}$ applies for the capillary pressure, we find the equivalent radius of a nucleus to be $5{\cdot}3 \times 10^{-8}$ cm. This is a quantity of molecular dimensions, and lends support to the view that a vapour contains a certain proportion of coaggregated molecules which are capable of acting as nuclei for condensation.

109. Ebullition of Liquids.—It is frequently stated on the strength of the relations we have just deduced, that a bubble of radius r in a liquid will not expand indefinitely and rise to the surface as in ebullition until the vapour pressure p inside the bubble exceeds the external pressure p_1 by $\frac{2\gamma}{r}$. This neglects the effect of the gas contained in the bubble, which plays an important part in the phenomenon. If there were no gas in the bubble, it could not exist in stable equilibrium in the liquid, for if its radius r were such as to make $\frac{2\gamma}{r} + p'$ greater than p it would collapse entirely. Let us suppose that the bubble contains a certain amount of gas and that the temperature and external pressure remain constant. The partial pressure of the gas varies inversely as the volume of the bubble and may be represented by $\frac{a}{r^3}$. The radius of the bubble is then determined by the equation:

$$p + \frac{a}{r^3} = p' + \frac{2\gamma}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (241)$$

---

* Wilson, *Phil. Trans.*, 189, 265 (1897).

The equilibrium is always stable if p is less than p', for in this case $\frac{a}{r^3}$ is greater than $\frac{2\gamma}{r}$, and any alteration in the value of r will disturb the equilibrium in such a direction as to tend to make the bubble regain its former radius.

On the other hand, if p is greater than p' the equilibrium may be stable or unstable. To obtain the condition of neutral equilibrium differentiate equation (241) with respect to r and equate to zero. Thus:

$$a = \frac{2}{3}\gamma r^2.$$

Substituting this value of a in (241) we have:

$$p - p' = \frac{4}{3}\frac{\gamma}{r}, \qquad \text{. . . . . . (242)}$$

which gives the value of the excess pressure required in order that ebullition may begin. In other words, the temperature of a liquid containing bubbles of radius r will rise until the excess pressure given by equation (242) is reached, and ebullition will commence as soon as the excess pressure amounts to two-thirds of the capillary pressure, and will not be delayed until the full capillary pressure is reached, as might appear at first sight.

110. Surface Tension and Surface Energy.—In a number of textbooks the terms "surface tension" and "surface energy" are regarded as synonymous. It can easily be shown, however, that the surface energy is greater than the surface tension by a thermodynamical consideration of the problem.

In any small change of the surface, let the temperature change by dT and the area of the surface by da. The change in the internal energy of the surface is given by:

$$d\mathbf{E} = \left(\frac{d\mathbf{E}}{dT}\right)_a dT + \left(\frac{d\mathbf{E}}{da}\right)_T da,$$

$$= c\,dT + \psi\,da, \qquad \text{. . . . . . (243)}$$

where ψ is the total surface energy per unit area. Also the heat which must be supplied to accomplish this change is given by:

$$\delta\mathbf{q} = d\mathbf{E} + \delta\mathbf{W},$$

$$= d\mathbf{E} - \gamma\,da,$$

since the external work is all done in enlarging the film against the forces due to surface tension. Substituting in this equation for $d\mathbf{E}$, we have:

$$\delta \mathbf{q} = c dT + (\psi - \gamma)\, da,$$

or

$$d\mathbf{S} = \frac{c}{T} dT + \frac{1}{T}(\psi - \gamma)\, da.$$

But this is a perfect differential and therefore

$$\frac{d}{da}\left(\frac{c}{T}\right)_T = \frac{d}{dT}\left(\frac{\psi - \gamma}{T}\right)_a,$$

or

$$\left(\frac{dc}{da}\right)_T = T\frac{d}{dT}\left(\frac{\psi - \gamma}{T}\right)_a. \quad . \quad . \quad . \quad (244)$$

Applying the condition of a perfect differential to equation (243) we have:

$$\left(\frac{dc}{da}\right)_T = \left(\frac{d\psi}{dT}\right)_a,$$

which substituted into equation (244) reduces this to:

$$\left(\frac{d\psi}{dT}\right)_a = T\frac{d}{dT}\left(\frac{\psi - \gamma}{T}\right)_a,$$

or

$$\psi = \gamma - T\left(\frac{d\gamma}{dT}\right)_a.$$

For all liquids the surface tension decreases with increase of temperature, and therefore the total surface energy is greater than the surface tension. Thus it follows that if a film of liquid be suddenly increased in size it is cooled, for the work done in overcoming the surface tension is less than the increase in total surface energy which must take place at the expense of the internal energy.

CHAPTER XI

THE APPLICATION OF THERMODYNAMICS TO ELECTRICAL PHENOMENA

111. Thermoelectricity.—In 1822 Seebeck discovered that if a closed circuit be formed by joining the ends of two wires of different metals and the junctions maintained at different temperatures, an electric current passes round the circuit. He arranged a number of metals in a thermoelectric series such that, when any two comprise a circuit, the current flows across the hot junction from the metal occurring earlier in the series to that occurring later. In any such circuit if the junction which was formerly heated be cooled, and that which was cooled be heated, the current flows in the opposite direction to that previously, the effect, therefore, being reversible. It was at first considered that the electromotive force of such a circuit varied directly as the difference of temperature between the junctions, but the discovery by Cumming of thermoelectric inversion, or the change in the order of the metals in the thermoelectric series at different temperatures, showed that there was not a direct proportionality between E.M.F. and difference of temperature. Later and more accurate experiments have shown that, although for small differences of temperature the E.M.F. is approximately proportional to the difference of temperature, it can be represented with greater accuracy by an equation of the type:

$$X = at + bt^2,$$

where X is the E.M.F., t the difference of temperature, and a and b constants. This equation represents a parabola, with axis parallel to the axis of X, passing through the points $(0, 0)$ and $\left(-\frac{a}{b}, 0\right)$, and having a maximum value of X at $t = -\frac{a}{2b}$. This temperature is known as the neutral temperature.

The complementary phenomenon to the Seebeck effect was discovered in 1834 by Peltier*, who found that on passing a current across a junction of two dissimilar metals in one direction the junction was cooled, corresponding to the absorption of heat, whilst on reversal of the current heat was evolved and the junction warmed. The heat absorbed or evolved is found to be proportional to the quantity of electricity which passes the junction. The constant of proportionality is known as the Peltier coefficient for the two metals at the particular temperature, and we shall denote it by the symbol Π.

By the application of the laws of thermodynamics to the thermoelectric circuit it was shown by Lord Kelvin† that the Peltier effect is not the only source of electromotive force in such a circuit. Let us consider a circuit composed of two wires A and B, Fig. 41, the junctions being maintained at temperatures T_1 and T_2. Let X be the E.M.F. of the circuit, and we shall suppose that this arises solely from the Peltier effects at the two junctions. If a small quantity of electricity, Q, passes round the circuit the work done is XQ. Also during the process heat of amount $\Pi_1 Q$ is taken in at the hot junction and $\Pi_2 Q$ evolved at the cooler. The process, neglecting the irreversible Joule effect, which varies as the square of the current and can therefore be made small in comparison with the other effects for small currents, is reversible. Therefore by the first law:

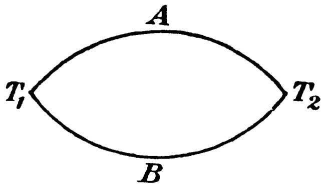

FIG. 41.

$$X = \Pi_1 - \Pi_2,$$

and by the second $\sum \frac{\delta q}{T} = 0$ for the cycle, so that

$$\frac{\Pi_1}{T_1} - \frac{\Pi_2}{T_2} = 0.$$

Hence

$$X = \Pi_2 \left(\frac{T_1 - T_2}{T_2} \right).$$

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* Peltier, *Ann. de Chim. et de Phys.*, 2^e Série, **56** (1834).

† Thomson, *Trans. R.S.E.* (1854).

Consequently, if our suppositions as to the origin of the E.M.F. in a thermoelectric circuit are correct, the E.M.F. should be proportional to the difference in temperature of the junctions. Experiment shows that this is not so. Lord Kelvin concluded that the Peltier effect cannot be the only source of electromotive force in the circuit, and suggested another existing between the different parts of the same metal at different temperatures. If a current passes along a wire whose temperature varies from point to point, this E.M.F. results in an absorption or evolution of heat which is known as the Thomson effect. Denoting by σ the E.M.F. in any substance due to unit difference of temperature between two points of it, $\int_{T_2}^{T_1} \sigma Q dT$ is the heat absorbed when a quantity of electricity Q passes from the point at temperature T_2 to that at T_1. The Thomson coefficient, σ, is a function of the temperature only, for if it depended on the cross-section of the wire or any other such variable a current might be maintained by the application of heat to a homogeneous metallic wire. Sometimes σ is called the specific heat of electricity in the given metal, for it is the heat absorbed by unit quantity of electricity through a rise of temperature of unity.

112. Theory of the Thermoelectric Circuit.—We are now in a position to consider the thermodynamics of the complete thermoelectric circuit. Using the same notation as before, the heat absorbed in taking a quantity Q of electricity round the thermoelectric current, Fig. 41, is:

$$Q \cdot \left\{ \Pi_1 - \Pi_2 + \int_{T_2}^{T_1} \sigma_A dT - \int_{T_2}^{T_1} \sigma_B dT \right\}.$$

Hence applying the two laws of thermodynamics:

$$X = \Pi_1 - \Pi_2 + \int_{T_2}^{T_1} (\sigma_A - \sigma_B) dT,$$

and

$$\frac{\Pi_1}{T_1} - \frac{\Pi_2}{T_2} + \int_{T_2}^{T_1} \frac{\sigma_A - \sigma_B}{T} dT = 0.$$

For a thermoelectric pair whose junctions are at temperatures T and $T + dT$, these equations become:

$$dX = d\Pi + (\sigma_A - \sigma_B)dT,$$

and

$$d\left(\frac{\Pi}{T}\right) + \frac{\sigma_A - \sigma_B}{T}dT = 0.$$

Combining these equations we obtain:

$$\Pi = T \cdot \frac{dX}{dT}, \qquad \ldots \ldots \quad (245)$$

and

$$\sigma_A - \sigma_B = - T\frac{d^2X}{dT^2}.$$

It was pointed out by Lord Kelvin that in order to justify the assumptions in the theory as developed above it would be necessary and sufficient to make experiments to verify quantitatively the relation (245). This was done by Jahn,* who enclosed various metallic junctions in a Bunsen ice calorimeter and observed the evolution of heat per hour with a current of about 1·6 amperes in either direction. The reversal of the current enabled the Joule effect to be eliminated. and the evolution of heat due to the Peltier effect alone to be obtained. The values of $\frac{dX}{dT}$ were determined for the same specimens, the rate of evolution of heat

TABLE XI.

Couple.	$\frac{dX}{dT}$ Microvolts per Degree.	$\Pi = T\frac{dX}{dT}$ Microvolts at 0° C.	Heat Calculated, Calories per Hour.	Heat Observed, Calories per Hour.
Cu-Ag ..	+ 2·12	+ 579	− 0·495	− 0·413
Cu-Fe ..	+ 11·28	+ 3,079	− 2·640	− 3·163
Cu-Pt ..	− 1·40	− 382	+ 0·327	+ 0·320
Cu-Zn ..	+ 1·51	+ 412	− 0·353	− 0·585
Cu-Cd ..	+ 2·64	+ 721	− 0·617	− 0·616
Cu-Ni ..	− 20·03	− 5,468	+ 4·680	+ 4·362

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* Jahn, *Wied. Ann.*, **34**, 755 (1888).

being calculated from these results on the assumption of equation (245) being exact. Table XI, page 204, gives the observed and calculated values of the rate of evolution of heat for various couples.

The agreement between the calculated and observed values must be regarded as satisfactory, considering the great difficulty in measuring such small quantities of heat.

113. Electrolysis.—If two platinum electrodes are put into an aqueous solution of a metallic salt and a source of electrical energy connected to these electrodes, it is found that the solution conducts electricity and undergoes decomposition; the products of the decomposition appear at the electrodes, and in many cases are gases. The electrodes by which the current enters and leaves the solution are termed the anode and cathode respectively.

Faraday investigated the phenomena of electrolysis very thoroughly and formulated the following generalisation.

"The quantity of a substance which separates at an electrode is proportional to the whole amount of electricity which passes, and to the chemical equivalent weight of the substance."

From this general law we see that when unit quantity of electricity (one coulomb) passes through an electrolyte, a definite quantity of substance will be set free, and the masses of different substances set free by the same quantity of electricity will be in the ratio of their chemical equivalent weights. The mass, in grams, of a substance set free by the passage of unit quantity of electricity is known as the electro-chemical equivalent. Having found the electro-chemical equivalent of one element that of any other can be found by multiplying by the ratio of the chemical equivalents. The electro-chemical equivalent of silver has been determined with great accuracy, and found to be 0·0011183 gram per coulomb.

As unit quantity of electricity liberates quantities of substances whose masses are in the same ratio as their chemical equivalents, it follows that a certain definite quantity of electricity is needed to liberate one gram equivalent of any substance. Now one coulomb liberates 0·0011183 gram of silver whose chemical equivalent is 107·88, so the quantity of electricity necessary to deposit one gram equivalent is $\frac{107\cdot 88}{0\cdot 0011183}$, or 96,470 coulombs.

For most practical purposes the figure 96,500 coulombs is sufficiently accurate. This quantity is usually denoted by the letter $\boldsymbol{F}$, and Faraday's results can be expressed mathematically by the equation:

$$w = \frac{a}{n\boldsymbol{F}} \cdot Q,$$

where w is the mass in grams of substance set free by the passage of Q coulombs of electricity, and a is the atomic weight of the element of valency n. It will be seen that $\frac{a}{n\boldsymbol{F}}$ is what we have previously called the electro-chemical equivalent.

114. The Ionic Hypothesis.—The phenomena of electrolysis can be explained by the ionic hypothesis of Arrhenius. According to this hypothesis any acid, base, or salt when dissolved in water splits up into ions which carry either a positive or negative electric charge. The solution as a whole has no resulting charge, for that on the positive ions just annuls that on the negative ions. In solutions of moderate strength, only a fraction of the molecules of electrolyte are split up into ions; this fraction is termed the degree of ionisation. Dilution of the solution increases the degree of ionisation, and at infinite dilution all the molecules are ionised. Measurements of the conductivity of solutions enable the degree of ionisation to be found experimentally.

If two electrodes are put into a solution of an electrolyte the ions with a negative charge move towards the anode, and are therefore termed anions, whilst those with a positive charge move towards the cathode and are termed cations. Let us consider the case of the electrolysis of a solution of copper sulphate. This salt splits up into the ions Cu^{++} and SO_4^{--}, the $++$ and $--$ signs denoting that two positive and two negative charges are carried by the cation and anion respectively. When the cation reaches the cathode it is there deposited; the anion, however, on reaching the anode has its charge annulled and combines with the hydrogen of the water to form sulphuric acid and liberates oxygen. If the anode were made of copper there would be no gas liberated, the anion combining with the copper of the electrode and going into solution again as copper sulphate. The net result of the electrolysis in this case would be a transfer of copper from the anode to the cathode.

So far we have said nothing of the velocities with which the ions travel. If the ions are associated with equal amounts of salt and move with equal velocities, on passing a current through the solution the middle portion will remain unaltered in composition, whilst the products of decomposition will be taken in equal proportions from the solution surrounding the anode and that surrounding the cathode. If, as is more usual, the anions and cations have different velocities, the faster moving of the two will leave the portion of the solution whence it comes more quickly than the other ion enters. Hence with non-dissolvable electrodes the concentration of the solution round one electrode will decrease more rapidly than round the other.

Suppose we have a cell containing a solution of an electrolyte fitted up with the anode on the left and the cathode on the right, both of non-dissolvable material. Distances measured from left to right will be considered positive, and the velocity of the cation we shall denote by α and of the anion by $-\beta$. These velocities can be resolved into the components:

$$\tfrac{1}{2}(\alpha+\beta)+\tfrac{1}{2}(\alpha-\beta) \quad \text{and} \quad -\tfrac{1}{2}(\alpha+\beta)+\tfrac{1}{2}(\alpha-\beta),$$

respectively. On pairing these components we see that the effect is the same as if the cations moved with the velocity $\frac{1}{2}(\alpha+\beta)$ and the anions with velocity $-\frac{1}{2}(\alpha+\beta)$, involving no accumulation at the electrodes, and a steady drift of the electrolyte itself without separation with velocity $\frac{1}{2}(\alpha-\beta)$. The net result is a gain of electrolyte at the cathode of $\frac{1}{2}(\alpha-\beta)$, and a loss due to electrolytic separation of $\frac{1}{2}(\alpha+\beta)$, making together a total loss of β. Similarly at the anode there is a total loss of α. As the metal deposited on the cathode is proportional to $(\alpha+\beta)$ the ratio of the mass of metal contained in the salt molecules carried away from the cathode space to the mass of metal deposited is $\dfrac{\beta}{\alpha+\beta}\cdot$ The ratio of the mass of metal contained in the salt molecules carried away from the anode space to the mass of metal deposited is $\dfrac{\alpha}{\alpha+\beta}\cdot$

In the case of a dissolvable anode the metal going into solution is proportional to $(\alpha+\beta)$, and there is a net gain at the anode of β, and the ratio of the mass of metal in the salt molecules gained at the anode to the mass of metal deposited at the cathode is $\frac{\beta}{\alpha + \beta}$, which is the same as the ratio of loss at the cathode.

115. Reversible and Irreversible Cells.—The various types of cell used for the production of electric currents are not all reversible. Consider, for instance, the Volta cell. This consists of a plate of copper and a plate of zinc in dilute sulphuric acid. When the cell is delivering electrical energy the zinc goes into solution and hydrogen is evolved at the copper electrode, the current passing through the electrolyte from zinc to copper. If a current from an external source is passed through the cell in the reverse direction, copper is dissolved and hydrogen evolved at the zinc electrode. A reversal of current does not restore the initial state of the cell, which is, therefore, irreversible.

The Daniell cell in its simplest form consists of a glass jar in which is stood a porous pot containing a rod of zinc and dilute sulphuric acid or a solution of zinc sulphate. Outside the porous pot is a copper plate in a saturated solution of copper sulphate. When the cell is working zinc sulphate is formed, the copper sulphate decomposed and copper deposited. On passing a current from an external source through the cell in the reverse direction, that is, so that the current goes through the electrolyte from copper to zinc, the deposited copper redissolves and zinc is deposited from the zinc sulphate solution; a reversal of current in this case restores the initial conditions. This cell is reversible.

In 1851 Lord Kelvin calculated the E.M.F. of a Daniell cell on the assumption that the electrical energy arises solely from the chemical changes occurring in the cell. Thus, if ΔH is the total heat of reaction, when a quantity of electricity nF is taken from the cell whose E.M.F. is X, we have:

$$nFX = -\Delta H,$$

or

$$X = \frac{-\Delta H}{nF}.$$

Now the heat of formation of zinc sulphate per gram molecule is 37,730 calories, and the heat of decomposition of copper sulphate 12,400 calories, the total heat of reaction for the passage of $2F$

coulombs being, therefore, 50,130 calories. Hence the E.M.F. of a Daniell cell is given by:

$$X = \frac{50{,}130 \times 4\cdot 185 \times 10^7}{2 \times 96{,}500 \times 10^{-1}} \text{ c.g.s. units,}$$

$$= \frac{50{,}130 \times 4\cdot 185}{2 \times 96{,}500} \text{ volts,}$$

$$= 1\cdot 09 \text{ volts,}$$

a result which agrees well with the experimental value, which ranges from 1·07 to 1·14 volts, depending upon the concentrations of the solutions.

It was pointed out by Helmholtz that the E.M.F. of a cell might be dependent upon the thermal E.M.F.s in the cell in addition to the heat of reaction, and that in this case the simple equation of Lord Kelvin would be incorrect. We can obtain an equation for the E.M.F., taking these effects into account, by considering the changes of internal energy and entropy in the cell.

When the cell under consideration is working, let the number of gram molecules simultaneously passing into the mass of each reactant be denoted by ν_1, ν_2 etc., as before. The change of internal energy when nF units of electricity pass through the cell is

$$\Delta H - p\Sigma \nu_1 v_1,$$

the pressure and temperature being constant, and ΔH the heat of reaction under these conditions. Hence

$$\left(\frac{d\mathbf{E}}{dQ}\right)_T = \frac{\Delta H}{nF} - p\,\frac{\Sigma \nu_1 v_1}{nF}.$$

For any small change when the temperature changes by dT and the cell delivers dQ units, the change in internal energy is given by:

$$d\mathbf{E} = \left(\frac{d\mathbf{E}}{dT}\right)_Q dT + \left(\frac{d\mathbf{E}}{dQ}\right)_T dQ, \quad . \quad . \quad . \quad (246)$$

it being understood that the differential coefficients relate to constant pressure conditions. Under the same conditions the change in volume of the system, $d\mathbf{v}$, is given by:

$$d\mathbf{v} = \frac{\Sigma\nu_1 v_1}{nF}\,dQ + \Sigma\nu_1\left(\frac{dv_1}{dT}\right)_Q dT.$$

Since

$$\delta\mathbf{q} = d\mathbf{E} + \delta\mathbf{W},$$

and the external work for the system is done by the passage of electricity and by volume changes, we have in this case:

$$\delta\mathbf{q} = \left(\frac{d\mathbf{E}}{dT}\right)_Q dT + \left(\frac{d\mathbf{E}}{dQ}\right)_T dQ + XdQ + pd\mathbf{v};$$

or

$$d\mathbf{S} = \frac{1}{T}\left\{\left(\frac{d\mathbf{E}}{dQ}\right)_T + X\right\} dQ + \frac{1}{T}\left(\frac{d\mathbf{E}}{dT}\right)_Q dT + \frac{p}{T}\,d\mathbf{v}$$

$$= \frac{1}{T}\left\{\left(\frac{d\mathbf{E}}{dQ}\right)_T + X + p\,\frac{\Sigma\nu_1 v_1}{nF}\right\}dQ + \frac{1}{T}\left\{\left(\frac{d\mathbf{E}}{dT}\right)_Q + p\Sigma\nu_1\left(\frac{dv_1}{dT}\right)\right\}_Q dT.$$

This is a perfect differential, so that:

$$\frac{d}{dT}\left\{\frac{1}{T}\left(\frac{d\mathbf{E}}{dQ}\right)_T + \frac{X}{T} + \frac{p}{T}\,\frac{\Sigma\nu_1 v_1}{nF}\right\} = \frac{d}{dQ}\left\{\frac{1}{T}\left(\frac{d\mathbf{E}}{dT}\right)_Q + \frac{p}{T}\Sigma\nu_1\left(\frac{dv_1}{dT}\right)_Q\right\} \quad (247)$$

Applying the condition for a perfect differential to equation (246) we have:

$$\frac{d}{dQ}\left(\frac{d\mathbf{E}}{dT}\right) = \frac{d}{dT}\left(\frac{d\mathbf{E}}{dQ}\right)$$

$$= \frac{d}{dT}\left\{\frac{\Delta H}{nF} - p\,\frac{\Sigma\nu_1 v_1}{nF}\right\}.$$

Substituting in equation (247) we have:

$$\frac{d}{dT}\left\{\frac{1}{T}\left(\frac{\Delta H}{nF}-p\frac{\Sigma\nu_1 v_1}{nF}\right)+\frac{X}{T}+\frac{p}{T}\frac{\Sigma\nu_1 v_1}{nF}\right\}$$
$$=\frac{1}{T}\frac{d}{dT}\left\{\frac{\Delta H}{nF}-p\frac{\Sigma\nu_1 v_1}{nF}\right\}+\frac{p}{T}\frac{d}{dQ}\Sigma\nu_1\left(\frac{dv_1}{dT}\right)_Q,$$

or

$$X=-\frac{\Delta H}{nF}+T\frac{dX}{dT}. \quad . \quad . \quad . \quad . \quad (248)$$

A similar equation could be obtained more simply by considering changes at constant volume. In that case ΔH would have to be replaced by ΔE, the heat of reaction at constant volume. When the reactants in the cell are present in solid or liquid form there is very little difference between ΔH and ΔE, and hence the electromotive force under constant volume conditions will be approximately equal to that at constant pressure.

The temperature coefficient of the Daniell cell is negligible, and this accounts for the result obtained by Lord Kelvin being so near the experimental value.

116. Concentration Cells.—An electromotive force is produced whenever there is a difference of any kind at two electrodes immersed in electrolytes. In the more familiar type of cell, such as a Daniell cell or Bichromate cell, the difference is produced by the use of dissimilar electrodes, but an electromotive force may be obtained by the use of two electrodes of the same material placed in solutions of different substances, or in differently concentrated solutions of the same substance. Any cell which is capable of the production of electrical energy by the use of different concentrations is termed a concentration cell. It must be noticed that in this type of cell the electrical energy is obtained from the energy of expansion of substances from greater to smaller concentrations, and not from chemical changes.

(i) *Liquid Concentration Cells.*—Suppose we have a liquid concentration cell of the type:

Metal M/Solution of MA (concentration c_1)/Solution of MA (concentration c_2)/Metal M.

The letter M is supposed to represent the basic radical and A the acid radical, *e.g.* for silver nitrate, M would be the Ag radical and A the NO_3 radical. When such a cell is in action the current flows through the electrolyte from the less to the more concentrated solution and tends to equalize them.

In order to apply the laws of thermodynamics to the production of an E.M.F. by a concentration cell it is necessary to find a reversible means of keeping the solutions at their original concentrations. We shall suppose that in each case the solutions are contained in cylinders fitted with semi-permeable pistons through which the solvent but not the solute can pass, so that when electrical energy is being taken from the cell the concentration of the stronger solution is maintained by expelling solvent through one semi-permeable piston, and that of the weaker by allowing the solvent to enter by the other semi-permeable piston.

On the passage of a quantity dQ of electricity it will be seen, by the aid of sections 113 and 114, that the weaker solution surrounding the anode gains $\frac{dQ}{nF} \cdot \frac{\beta}{\alpha + \beta} = dN$ gram molecules of the solute, whilst the stronger solution surrounding the cathode loses an equal amount. To maintain the concentrations of the solutions at their original values work of amount $P_1 dV_1$ is done against the osmotic pressure in the case of the stronger solution, and $P_2 dV_2$ by the osmotic pressure in the weaker solution, where P_1 and P_2 are the osmotic pressures of the solutions of concentrations c_1 and c_2, and dV_1 and dV_2 are the volumes of solvent containing dN gram molecules of solute in the two cases. If the solutions are dilute:

$$P_1 dV_1 = P_2 dV_2.$$

After the passage of the quantity dQ of electricity there is more of the weaker solution and less of the stronger. To restore the cell to its initial condition the excess of weaker solution is separated from the rest and solvent expelled until it is of the same concentration as the stronger solution when it is returned to it. The cell has now been returned to its initial condition by means of an isothermal reversible cycle, so the total external work done is zero.

The work done in concentrating the excess of weaker solution is:

$$\int_{c_1}^{c_2} PdV,$$

where P is the osmotic pressure of the solution and the integral has to be evaluated between the limits of concentration c_1 and c_2. This work must be equal to the electrical work, or

$$XdQ = \int_{c_1}^{c_2} PdV, \quad . \quad . \quad . \quad . \quad . \quad . \quad (249)$$

where X is the E.M.F. of the cell. In the case of dilute electrolytes the osmotic pressure is increased above its normal value in the ratio $x : 1$, where x is the number of ions given by one molecule of the electrolyte. Hence

$$P = xc\boldsymbol{R}T.$$

Also by the definition of c we have:

$$c = \frac{dN}{V},$$

and therefore

$$dV = -\,dN \cdot \frac{dc}{c^2}.$$

Substituting for P and dV in equation (249), this becomes:

$$XdQ = x\boldsymbol{R}TdN \int_{c_2}^{c_1} \frac{dc}{c},$$

$$= x \cdot \frac{\beta}{\alpha + \beta} \cdot \frac{\boldsymbol{R}T}{n\boldsymbol{F}} \cdot dQ \log \frac{c_1}{c_2},$$

or

$$X = x \cdot \frac{\beta}{\alpha + \beta} \cdot \frac{RT}{nF} \cdot \log \frac{c_1}{c_2} \quad . \quad . \quad . \quad . \quad (250)$$

(ii) *Gas Concentration Cells.*—An electromotive force may be produced by using the same strength solution throughout the cell and having electrodes of different concentrations. The most familiar cell of this description is the gas concentration cell. A simple type is shown in Fig. 42. It consists of two platinised platinum electrodes A and B, each sealed into the top of a glass vessel. The upper part of each vessel contains a gas, whilst the lower part contains a dilute acid which extends from one electrode to the other in a wider vessel as shown. The situation of each electrode is such that it is partly surrounded by acid and partly by the gas. If the gas pressures in A and B are not equal, being p_1 and p_2 respectively, the cell will have a potential difference between the electrodes. When the cell is delivering electrical energy gas will be taken into the platinised platinum at A, passed through the solution, and given up at B.

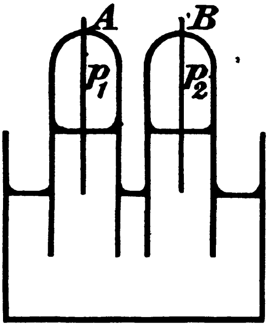

FIG. 42.
A Gas Concentration Cell.

Suppose we take energy from the cell and keep the pressure of the gas at each electrode constant by means of pistons working in cylinders, one attached to each electrode vessel. Let v_1 be the volume of gas at pressure p_1, which disappears from A, and v_2 at pressure p_2 be that which appears at B, when a quantity of electricity, dQ, is taken from the cell in a reversible manner. The mass of gas disappearing at A and that appearing at B are equal and, for given pressures, the action is reversible, the E.M.F. required to produce the reverse effect being X, the E.M.F. of the cell. The work done by the cell in this first process is:

$$XdQ + p_2v_2 - p_1v_1.$$

The cell can be restored to its initial condition by isolating the gas which has appeared at B and compressing it at constant temperature until it occupies a volume v_1 at pressure p_1, and then restoring it to the gas surrounding the electrode at A. The work done on the gas in this process is:

$$\int_{v_1}^{v_2} pdv.$$

As the net work obtainable in a reversible isothermal cycle is zero, we have:

$$XdQ + p_2v_2 - p_1v_1 = \int_{v_1}^{v_2} pdv,$$

or

$$XdQ = \int_{p_2}^{p_1} vdp. \quad . \quad . \quad . \quad . \quad . \quad . \quad (251)$$

If each gram molecule of the gas on going into solution gives rise to x gram ions, each of valency n, the passage of a quantity dQ of electricity will transfer $\frac{dQ}{xnF}$ gram molecules of gas from A to B. For this mass of gas we have:

$$pv = \frac{dQ}{xnF}RT,$$

and substituting in equation (251), this reduces to:

$$XdQ = \frac{dQ}{xnF} . RT\int_{p_2}^{p_1} \frac{dp}{p}$$

or

$$X = \frac{RT}{xnF} \log \frac{p_1}{p_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (252)$$

117. The Mechanism of Current Production in Solutions.—The mechanism of the production of potential differences between a metal and a solution in which it is immersed has been explained by Nernst* by a theory of solution pressure.

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* Nernst, *Zeit. phys. Chem.*, **2**, 613 (1888); **4**, 129 (1889); and *Wied. Ann.*, **45**, 360 (1892).

According to this hypothesis all metals possess a solution pressure which tends to drive positively charged ions from the metal into the solution. When some positive ions have left the metal it will be left with a negative charge. It might at first appear that ions would be able to go on leaving the metal for an indefinite period, but owing to the negative charge left on the metal by the departure of the ions there is an electrostatic field set up between the metal and those ions which have gone into solution, which makes the further expulsion of ions increasingly difficult.

If the solution happens to contain the same kind of ions as are driven out of the metal there will be a tendency on their part, owing to the osmotic pressure, to drive themselves on to the metal. When equilibrium is established the solution pressure of the ions in the metal is balanced by the osmotic pressure of the ions in solution and the electrostatic field. Sometimes the osmotic pressure of the ions in solution is sufficiently great to overcome the solution pressure of the ions in the metal. When this occurs the ions deposit themselves on the metal, which in consequence becomes positively charged with respect to the solution.

Let us consider a metal immersed in a solution containing the same ions as are expelled from the metal. We shall suppose that the system is in equilibrium, and that the metal is electrically positive to the solution. Now let a small virtual change take place by which dN gram ions, carrying an electrical charge dQ, leave the metal. The electrical work done by the system is XdQ. In addition there is the work done in bringing the dN gram ions from the solution pressure p to the osmotic pressure P. This work is:

$$\int_p^P pdv = dN \, . \, \mathbf{R}T \log \frac{p}{P},$$

if we assume the perfect gas laws to be applicable to the ions. As the system is in equilibrium we have, by the principle of virtual work,

$$XdQ + dN\mathbf{R}T \log \frac{p}{P} = 0,$$

and since

$$\frac{dQ}{dN} = n\mathbf{F},$$

this reduces to

$$X = \frac{RT}{nF} \log \frac{P}{p}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (253)$$

In a similar manner we are able to calculate the potential difference existing at the surface of separation of two solutions of different concentrations.

We shall suppose that one molecule of the salt on going into solution forms one cation and $(x - 1)$ anions, making x ions in all. Now suppose a quantity of electricity dQ passes across the surface of contact of the two solutions in the direction from the solution of concentration c_1 to that of concentration $c_2 (c_1 > c_2)$. In this process $\frac{dQ}{nF}\frac{\alpha}{\alpha + \beta}$ gram cations pass in the same direction and $\frac{dQ}{nF} . (x - 1) . \frac{\beta}{\alpha + \beta}$ gram anions in the opposite. As the cations pass from the concentration c_1 to c_2 they do work in expansion of amount $RT . \frac{dQ}{nF} . \frac{\alpha}{\alpha + \beta} \log \frac{c_1}{c_2}$, whilst the anions require an amount of work $RT . \frac{dQ}{nF} . (x - 1) . \frac{\beta}{\alpha + \beta} \log \frac{c_1}{c_2}$ to be done upon them. Hence the total work obtainable from the energy of expansion is:

$$RT . \frac{dQ}{nF}\left\{\frac{\alpha - (x - 1)\beta}{\alpha + \beta}\right\} \log \frac{c_1}{c_2},$$

and this must be equal to the electrical work XdQ. Hence

$$X = \frac{RT}{nF}\left\{\frac{\alpha - (x - 1)\beta}{\alpha + \beta}\right\} \log \frac{c_1}{c_2}. \quad . \quad . \quad . \quad . \quad (254)$$

In a cell of the type:

Metal (M)/Solution of (MA (concentration c)/Solution of MA (concentration c_2)/Metal M.

the effective potential difference between the terminals will be the algebraic sum of three potential differences. Denoting these by X_1, X_2, and X_3 from left to right, and the potential difference between the terminals by X, we have, by equations (253) and (254),

$$\begin{aligned} X &= X_1 - X_2 - X_3, \\ &= \frac{RT}{nF}\log\frac{P_1}{p} - \frac{RT}{nF}\left\{\frac{a-(x-1)\beta}{a+\beta}\right\}\log\frac{c_1}{c_2} - \frac{RT}{nF}\log\frac{P_2}{p}, \\ &= \frac{RT}{nF}\left\{\log\frac{P_1}{P_2} - \left[\frac{a-(x-1)\beta}{a+\beta}\right]\log\frac{c_1}{c_2}\right\}. \end{aligned}$$

Since the osmotic pressures P_1 and P_2 are proportional to the concentrations c_1 and c_2 this can be written as:

$$\begin{aligned} X &= \frac{RT}{nF}\left\{1 - \left[\frac{a-(x-1)\beta}{a+\beta}\right]\right\}\log\frac{c_1}{c_2}, \\ &= x \cdot \frac{\beta}{a+\beta} \cdot \frac{RT}{nF} \cdot \log\frac{c_1}{c_2}, \end{aligned}$$

which is the same as equation (250).

When the electrolyte is not completely ionised c_1 and c_2 must be taken as the ionic concentrations. Let us consider the case of silver electrodes in aqueous solutions of silver nitrate. In this case $x = 2$, and the total valency of the cations or anions coming from one molecule of the salt is unity. Also the experimentally determined value of the transport number of the anion is 0·528. Hence the E.M.F. of this cell is given by:

$$X = 1{\cdot}056\,\frac{RT}{F}\log\frac{c_1}{c_2}.$$

There are several experimental methods by which the liquid/liquid potential difference may be eliminated. The commonest device is to interpose a saturated solution of ammonium nitrate or potassium chloride at the junction of the two liquids, which is supposed to have the effect of nullifying liquid potential differences. If such a device is used the equation for the E.M.F. of a cell such as we are considering becomes simply:

$$X = \frac{RT}{F}\log\frac{c_1}{c_2}.$$

Table XII, page 214, indicates the degree of agreement between the theoretical and experimental values. The experimental results are those of Abegg and Cumming,* who used a solution of ammonium nitrate to eliminate the liquid/liquid potential difference.

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* Abegg and Cumming, *Zeit. für Electrochemie*, **13**, 18 (1907).

TABLE XII.

Concentration of $AgNO_3$.	Ratio of the Ionic Concentration $\frac{c_1}{c_2}$	$\frac{RT}{F} \log \frac{c_1}{c_2}$	E.M.F. Observed.
$\frac{N}{10} : \frac{N}{100}$	9·0	0·0563 volt	0·0556 volt
$\frac{N}{100} : \frac{N}{1,000}$	9·6	0·0580 volt	0·0579 volt

118. The Discharge of Electricity from Hot Bodies.—It has been known for a considerable time that the air in the neighbourhood of hot bodies has the power of conducting electricity. A platinum wire maintained at a dull red heat in air will cause an electrode in its vicinity to acquire a positive charge of electricity which decreases in magnitude as the temperature of the wire is raised, becoming zero when this is at a white heat. If the experiment is performed in an enclosure where the pressure is very low, the maximum value of the positive charge on the electrode is reached at a lower temperature, and on raising the temperature of the wire above this value the positive charge decreases and ultimately changes sign; the magnitude of this negative charge increases progressively as higher temperatures are reached.

It is now definitely established that these phenomena are due to the discharge of positive and negative ions from the hot body. Experiment indicates that the positive ions are of metals and gases, traces of which are present as impurities in the specimens of wire used. The rate of discharge of positive ions diminishes with continued emission, but may be restored in a number of ways the mechanism of which is somewhat obscure. The negative ions are electrons. It is only with the emission of negative electricity that we shall deal.

When a hot body is enclosed in a vacuum a state of equilibrium is soon attained when electrons return to the hot body as fast as they are emitted. When this occurs the system is analogous to a liquid in contact with its vapour, and we can apply the Clapeyron equation. Thus we have:

$$\frac{l}{T} = (v_2 - v_1)\frac{dp}{dT},$$

where l may be regarded as the latent heat of vaporization of the electrons, $(v_2 - v_1)$ the change of volume of the system, and p the equilibrium pressure of the electrons. As v_1 is very small it can be neglected in comparison with v_2, and the Clapeyron equation becomes:

$$\frac{l}{T} = v\frac{dp}{dT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (255)$$

Now the electrons are extremely small particles, having a mass of only $\frac{1}{1850}$ that of a hydrogen atom, and as we shall suppose the concentration so small that the effects arising from the mutual repulsions of the electrons are negligible, it might reasonably be expected that an atmosphere of them would behave in the same manner as a gas. Consequently, applying the gas laws by equation (177) we can write the pressure exerted by the electrons as:

$$p = NkT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (177)$$

where N is the number of electrons per unit volume.

In order to remove an electron from the hot body a certain amount of work will have to be done. Denoting this work by Z, the change in energy corresponding to the "evaporation" of the electrons occupying a volume v will be NvZ, and an amount of external work pv will also be done against the external pressure. Hence the latent heat is given by:

$$l = NvZ + pv. \quad . \quad . \quad . \quad . \quad . \quad . \quad (256)$$

Combining equations (255) and (256), we have:

$$NvZ + pv = Tv\frac{dp}{dT},$$

or

$$NZ + p = T\frac{dp}{dT},$$

which on substitution for p from equation (177) becomes:

$$NZ = kT^2\frac{dN}{dT}. \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (257)$$

Integrating this equation:

$$N = N_1 e^{\int^T \frac{Z}{kT^2} dT}, \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (258)$$

where N_1 is an integration constant.

It can be shown* that for a gas in equilibrium the number of molecules returning to unit area per sec., N', is given by:

$$N' = N\sqrt{\frac{kT}{2\pi m}}, \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (259)$$

where m is the mass of a molecule.

Applying this result to the case of our "electron gas" we have, by combination of equations (258) and (259),

$$N' = N_1\sqrt{\frac{kT}{2\pi m}} \cdot e^{\int^T \frac{Z}{kT^2} dT},$$

as the number of electrons emitted per unit area of the hot body in one second. Multiplying each side of this equation by e, the charge carried by an electron, we obtain the current per unit area as:

$$i = N_1 e\sqrt{\frac{kT}{2\pi m}} \cdot e^{\int^T \frac{Z}{kT^2} dT}. \qquad . \quad . \quad . \quad . \quad . \qquad (260)$$

If it be assumed that Z is independent of the temperature the integration may be performed, and this equation becomes:

$$i = N_1 e\sqrt{\frac{kT}{2\pi m}} \cdot e^{-\frac{Z}{kT}},$$

which may be written:

$$i = AT^{\frac{1}{2}}e^{-\frac{b}{T}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (261)$$

119. The Variation of Z with Temperature.—There

---

[*] Jeans, *Dynamical Theory of Gases*, 2nd Edition, p. 133.

is thermodynamic evidence that Z is not independent of the temperature. The relationship between these two quantities can be found by the following thermodynamic proof, due to Richardson.*

Consider two conductors, A and A′, Fig. 43, of the same material maintained at temperatures T and T' respectively, and connected by a thin conductor of the same material covered with an insulating material impervious to electrons. Each conductor is surrounded by an evacuated chamber with insulating walls. Although A and A′ are connected by a conductor there will in general be a difference in potential between their respective surfaces on account of the difference of temperature. Let us suppose that the electric potentials of A and A′ when connected together are X and X' (X greater than X'). Surround A by an equipotential surface maintained at X'.

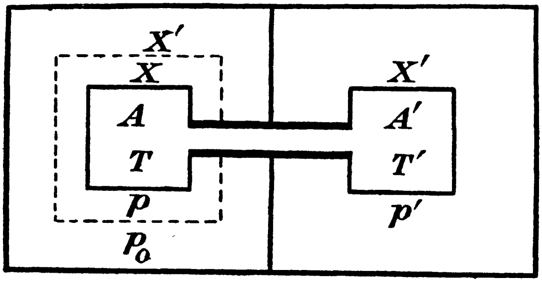

FIG. 43.

If one electron is transferred from near the surface of A to the exterior of the surface at potential X' which surrounds it, we have by the first law of thermodynamics:

$$e(X - X') = -\int_{\frac{1}{N}}^{\frac{1}{N_0}} pdv,$$

where p is the pressure exerted by the electrons and N and N_0 the concentrations within and without the equipotential surface surrounding A, the integral having to be evaluated between the assigned limits, since v, the volume occupied by one electron, is $\frac{1}{N}$. Substituting NkT for p and $-\frac{dN}{N^2}$ for dv the above equation becomes:

---

* Richardson, *Phil. Mag.*, 23, 602 (1912).

$$
\begin{aligned}
e(X-X') &= \int_{N}^{N_0} NkT\frac{dN}{N^2}, \\
&= kT\log\frac{N_0}{N}, \\
&= kT\log\frac{p_0}{p}, \quad . \quad . \quad . \quad . \quad . \qquad (262)
\end{aligned}
$$

where p is the pressure of the electrons characteristic of A at the temperature T, and p_0 that of the electrons outside the equipotential surface referred to.

Now let the following reversible cycle be performed.

(i) Let n electrons be taken from A and passed through the equipotential surface. In this process heat of amount $nZ - ne(X - X')$ is absorbed.

(ii) The electrons removed from A are now expanded adiabatically from the pressure and temperature p_0 and T to p_1 and T′ respectively. The expansion is then continued isothermally until the pressure falls to p', the equilibrium pressure of the electrons surrounding A′.

After the adiabatic expansion the pressure is given by equation (23a) as:

$$
p_1 = p_0\left(\frac{T'}{T}\right)^{\frac{\gamma}{\gamma-1}}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (263)
$$

γ being the ratio of the specific heats of the electrons at constant pressure and constant volume.

The heat absorbed in the isothermal expansion from p_1 to p' is:

$$
n\int_{\frac{1}{N_1}}^{\frac{1}{N'}} pdv = nkT'\log\frac{N_1}{N'}, = nkT'\log\frac{p_1}{p'}.
$$

Substituting for p_1 from equation (263) this expression reduces to:

$$
nkT'\log\frac{p_0}{p'}\left(\frac{T'}{T}\right)^{\frac{\gamma}{\gamma-1}}.
$$

(iii) Allow the n electrons to fall into A′ at the temperature T'. The heat given out is nZ'.

(iv) To complete the cycle pass the electrons from A′ to A by means of the conductor joining them. The heat absorbed is:

$$\boldsymbol{ne}\int_{T'}^{T}\sigma dT.$$

All the processes in this cycle having been performed reversibly, the change of entropy is zero. Hence:

$$\frac{nZ}{T}-\frac{\boldsymbol{ne}(X-X')}{T}+n\boldsymbol{k}\log\frac{p_0}{p'}\left(\frac{T'}{T}\right)^{\frac{\gamma}{\gamma-1}}-\frac{nZ'}{T'}+\boldsymbol{ne}\int_{T'}^{T}\sigma\frac{dT}{T}=0,$$

which on substitution for $\boldsymbol{e}(X-X')$ from equation (262) reduces to:

$$\boldsymbol{e}\int_{T'}^{T}\frac{\sigma}{T}\cdot dT-\boldsymbol{k}\log\frac{p_0}{p}+\frac{Z}{T}-\frac{Z'}{T'}+\boldsymbol{k}\log\frac{p_0}{p'}+\boldsymbol{k}\log\left(\frac{T'}{T}\right)^{\frac{\gamma}{\gamma-1}}=0,$$

or

$$\boldsymbol{e}\int_{T'}^{T}\frac{\sigma}{T}\cdot dT+\boldsymbol{k}\log\frac{p}{p'}+\frac{Z}{T}-\frac{Z'}{T'}+\boldsymbol{k}\cdot\frac{\gamma}{\gamma-1}\cdot\log\frac{T'}{T}=0,$$

or

$$\log p-\frac{\gamma}{\gamma-1}\log T+\frac{Z}{\boldsymbol{k}T}+\frac{\boldsymbol{e}}{\boldsymbol{k}}\int_{0}^{T}\frac{\sigma}{T}\cdot dT=B,$$

where B is independent of T. Differentiating this equation with respect to T, we have:

$$\frac{1}{p}\cdot\frac{dp}{dT}-\frac{\gamma}{\gamma-1}\cdot\frac{1}{T}-\frac{Z}{\boldsymbol{k}T^2}+\frac{1}{\boldsymbol{k}T}\cdot\frac{dZ}{dT}+\frac{\boldsymbol{e}}{\boldsymbol{k}}\cdot\frac{\sigma}{T}=0$$

and substituting from equation (177):

$$\frac{1}{N} \cdot \frac{dN}{dT} = \frac{1}{\gamma - 1} \cdot \frac{1}{T} + \frac{Z}{kT^2} - \frac{1}{kT} \cdot \frac{dZ}{dT} - \frac{e}{k} \cdot \frac{\sigma}{T}.$$

Substituting in this equation for $\frac{dN}{dT}$ from (257), it becomes:

$$\frac{dZ}{dT} = \frac{k}{\gamma - 1} - e\sigma. \quad . \quad . \quad . \quad . \quad . \quad (264)$$

It is improbable that σ in this equation has exactly the same value as the Thomson coefficient measured with voltaic currents. It can justifiably be assumed, however, that σ is of the same order of magnitude as the specific heat of electricity.

If γ is taken as $\frac{5}{3}$, the ratio of the specific heats of a monatomic gas, the value of $e\sigma$ is approximately one-tenth of $\frac{k}{\gamma - 1}$ when the value of σ for bismuth, which has the greatest known Thomson coefficient, is used. For other substances the Thomson coefficient has varying values, sometimes positive and sometimes negative. It is evident that $e\sigma$ will in general be small in comparison with $\frac{k}{\gamma - 1}$, and the major part of the variation of Z with T will be determined by the first term on the right-hand side of equation (264). Hence as a first approximation, putting $e\sigma = 0$, and taking γ as $\frac{5}{3}$, we have:

$$\frac{dZ}{dT} = \tfrac{3}{2}k,$$

and integrating

$$Z = Z_0 + \tfrac{3}{2}kT.$$

Substituting this value of Z in equation (260), and performing the integration, the current per unit area is given by:

$$i = CT^2 e^{-\frac{d}{T}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (265)$$

where C and d are both independent of T.

According to equation (261), a straight line should be obtained by plotting $\log_{10} i - \frac{1}{2} \log_{10} T$ against T^{-1}, and according to (265) the same result should follow by plotting $\log_{10} i - 2 \log_{10} T$ against T^{-1}.

The following table gives the values found by Schlichter* for the total current from platinum wires. These have been plotted according to equations (261) and (265) in curves I and II, Fig. 44.

TABLE XIII.

T.	$i \times 10^8$ Amps.	$\frac{10^4}{T}$	$\log_{10} i - \frac{1}{2} \log_{10} T + 11$.	$\log_{10} i - 2 \log_{10} T + 15$.
1,195	0·15	8·37	0·637	0·020
1,211	0·42	8·26	1·082	0·456
1,227	0·78	8·15	1·348	0·712
1,243	1·35	8·05	1·584	0·943
1,259	2·47	7·94	1·843	1·193
1,275	4·17	7·85	2·067	1·408
1,291	6·3	7·75	2·245	1·580
1,307	9·9	7·66	2·438	1·764
1,323	15·75	7·56	2·636	1·953
1,339	27·5	7·47	2·877	2·188
1,355	47	7·38	3·106	2·408
1,371	76	7·29	3·313	2·609
1,387	106	7·21	3·455	2·742
1,403	168	7·13	3·652	2·933
1,419	268	7·04	3·852	3·124
1,435	400	6·97	4·024	3·290
1,451	550	6·89	4·159	3·416
1,467	785	6·82	4·312	3·563
1,483	1,090	6·75	4·452	3·694
1,499	1,430	6·67	4·566	3·799

It will be seen that either equation is capable of representing the experimental results with a fair degree of accuracy. Equation (265) is, however, more satisfactory from a theoretical standpoint and may be regarded as nearer to the truth than equation (261).

120. The Thermodynamics of Magnetisation.†—Consider unit mass of magnetic material in a magnetic field of strength F. The specific intensity of magnetisation of the body, i.e. the magnetic moment per unit mass, will be denoted by σ. In any small change in the system the external work done will be the difference between that done by the system by means of volume changes and that done on the system by magnetic changes. It can be shown that the latter may be represented by $Fd\sigma$. The expression for the first and second laws in the case of reversible changes, therefore, takes the form:

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* Schlichter, *Ann. der Phys.*, 47, 573 (1915).

† Stoner, *Phil. Mag.*, **19**, 565 (1935), and **23**, 833 (1937); Guggenheim, *Proc. Roy. Soc. A.*, **155**, 70 (1936).

$$TdS = dE_1 + pdv - Fd\sigma, \quad . \quad . \quad . \quad . \quad (266)$$

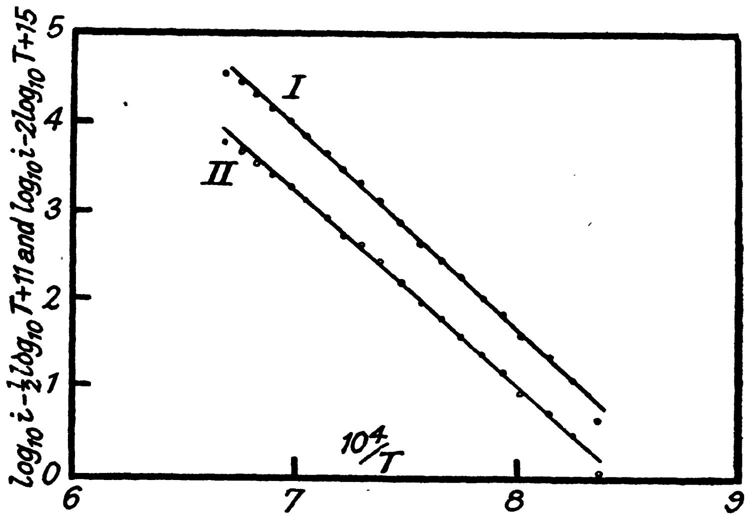

FIG. 44.

where dE_1 represents the change in internal energy.

In practice it is either changes at constant volume or at constant pressure that are dealt with. In the case where the volume is held constant the previous equation may be written:

$$TdS = dE_1 - Fd\sigma,$$

where all the variations refer to changes at constant volume.

If now the functions $H_1 = (E_1 - F\sigma)$, $A_1 = (E_1 - TS)$, $G_1 = (E_1 - TS - F\sigma)$ are formed, we have, still at constant volume:

$$\left.\begin{aligned} dE_1 &= TdS + Fd\sigma \\ dA_1 &= -SdT + Fd\sigma \\ dH_1 &= TdS - \sigma dF \\ dG_1 &= -SdT - \sigma dF \end{aligned}\right\} \text{applicable at constant volume.}$$

If instead of the functions E_1, H_1, etc., we form the functions $E_2 = (E_1 + pv)$, $H_2 = (H_1 + pv)$, etc., a series of equations such as

$$dE_2 = TdS + Fd\sigma,$$

which are applicable at constant pressure, may be obtained by substitution from equation (266).

It will be noticed that the form of the equations applicable at constant pressure and at constant volume respectively are the same. Applying the condition for a perfect differential to either series of equations we obtain:

$$\left.\begin{aligned} \left(\frac{dT}{d\sigma}\right)_S &= \left(\frac{dF}{dS}\right)_\sigma \\ \left(\frac{dS}{d\sigma}\right)_T &= -\left(\frac{dF}{dT}\right)_\sigma \\ \left(\frac{dT}{dF}\right)_S &= -\left(\frac{d\sigma}{dS}\right)_F \\ \left(\frac{dS}{dF}\right)_T &= \left(\frac{d\sigma}{dT}\right)_F \end{aligned}\right\} \quad \ldots\ldots \quad (267)$$

These equations correspond to the four thermodynamic relations of Maxwell. An important limitation must be noted however. Thus, since the relations are valid either at constant pressure or constant volume, the first equation may be written as

$$\left(\frac{dT}{d\sigma}\right)_{S,v} = \left(\frac{dF}{dS}\right)_{\sigma,v},$$

or

$$\left(\frac{dT}{d\sigma}\right)_{S,p} = \left(\frac{dF}{dS}\right)_{\sigma,p};$$

but this does not imply that $\left(\frac{dT}{d\sigma}\right)_{S,v}$, for example, is necessarily even approximately equal to $\left(\frac{dT}{d\sigma}\right)_{S,p}$. It may be shown,* however, that in the applications of these equations ordinarily made, it is unnecessary to distinguish between changes at constant pressure and those at constant volume. This cannot be decided upon thermodynamic grounds only, but is arrived at by a consideration of experimental results. In effect this means that volume changes may be neglected in comparison with the other changes occurring in the system.

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* Stoner, *loc. cit.*

The magnetisation may be represented generally as a function of the field and temperature, such as

$$\sigma = f(F, T).$$

The form of the function can be determined in special cases by making assumptions as to the dependence of the internal energy E_1 upon σ.

I. DIAMAGNETICS

Starting with the assumption:

$$\left(\frac{dE_1}{d\sigma}\right)_T = F,$$

we have from equations (267)

$$\begin{aligned}\left(\frac{d\sigma}{dT}\right)_F &= \left(\frac{dS}{dF}\right)_T \\ &= \frac{1}{T}\left(\frac{dE_1}{dF}\right)_T - \frac{F}{T}\left(\frac{d\sigma}{dF}\right)_T \\ &= \frac{1}{T}\left(\frac{dE_1}{d\sigma}\right)_T \cdot \left(\frac{d\sigma}{dF}\right)_T - \frac{F}{T}\left(\frac{d\sigma}{dF}\right)_T \\ &= 0.\end{aligned}$$

Thus $\sigma = f(F)$.

For a substance for which σ is proportional to F the susceptibility $\left(\frac{\sigma}{F}\right)$ is independent of the temperature. This corresponds to the observed characteristics of normal diamagnetic substances.

II. PARAMAGNETICS.

Starting with the assumption:

$$\left(\frac{dE_1}{d\sigma}\right)_T = 0,$$

we have from equations (267):

$$\left(\frac{d\sigma}{dT}\right)_F = \left(\frac{dS}{dF}\right)_T$$

$$= \frac{1}{T}\left(\frac{dE_1}{dF}\right)_T - \frac{F}{T}\left(\frac{d\sigma}{dF}\right)_T$$

$$= \frac{1}{T}\left(\frac{dE_1}{d\sigma}\right)_T \cdot \left(\frac{d\sigma}{dF}\right)_T - \frac{F}{T}\left(\frac{d\sigma}{dF}\right)_T,$$

$$= -\frac{F}{T}\left(\frac{d\sigma}{dF}\right)_T.$$

A solution of this equation is:

$$\sigma = f\left(\frac{F}{T}\right).$$

If at constant temperature it is known that σ is proportional to F, we then have:

$$\left(\frac{\sigma}{F}\right) = \left(\frac{C}{T}\right),$$

where C is a constant. This is Curie's law for paramagnetics.*

III. MAGNETO-CALORIC EFFECT.

If the state of magnetisation of a body is changed adiabatically it is found to be accompanied by a reversible temperature change. Although the effect has been known for a long time, it has recently attained a much greater importance owing to a suggestion by Debye, and independently by Giaugue, that use might be made of the effect for the attainment of extremely low temperatures.

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* Curie, *Ann. de Chimie* (1895).

The theory of the effect is quite straightforward. From equations (267) we have:

$$\begin{aligned}\left(\frac{dT}{dF}\right)_S &= -\left(\frac{d\sigma}{dS}\right)_F \\ &= -\left(\frac{d\sigma}{dT}\right)_F \cdot \left(\frac{dT}{dS}\right)_F \\ &= -\frac{T}{c_F}\cdot\left(\frac{d\sigma}{dT}\right)_F,\end{aligned}$$

where c_F is the specific heat of the body as measured at constant field strength.

To give an indication of the order of magnitude of the effect let it be supposed that for a particular substance Curie's law is followed in the form

$$\frac{\sigma}{F} = \frac{C}{T}.$$

Then
$$\left(\frac{d\sigma}{dT}\right)_F = -\frac{CF}{T^2}$$

and
$$\left(\frac{dT}{dF}\right)_S = \frac{CF}{c_F T}.$$

It will be seen from this approximate equation that at low temperatures, where c_F is very small, the lowering of temperature producable by suddenly diminishing a strong field to zero value should be relatively large.

Many difficulties have occurred in utilising this method for the production of low temperatures. Direct investigations have shown that at these low temperatures the specific heat is anomalous for certain substances, increasing as the temperature falls. Fortunately, however, it is found that the Curie law holds even in this anomalous specific heat region, and the temperatures reached by the adiabatic demagnetisation method have been determined by extrapolation on the basis of this law. Using mixed alums, $K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$ and 14·4 parts of $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$, Wiersma and de Haas have reached a temperature of 0·0044° K.

CHAPTER XII

THE THERMODYNAMICS OF RADIATION

121. Temperature Radiation.—The three processes by which a body may lose heat are convection, conduction, and radiation. For the first two of these processes to take place a material medium is required, but heat radiation is of the same nature as visible light, being an electromagnetic disturbance propagated through empty space with the velocity 3×10^{10} cm. per second.

If a body is maintained at a constant temperature, and continuously emits radiation without undergoing any change of structure, the radiation is called pure temperature radiation. At a low temperature a body emits radiation which is principally of long wave-length, but as the temperature is raised the proportion of shorter wave-length radiation increases. This radiation becomes apparent as visible light when the body is red hot. Further elevation of the temperature increases the proportion of short wave-length radiation, the body ultimately becoming white hot and emitting radiations of all visible wave-lengths. The character of the radiation emitted, i.e. the distribution of energy amongst the various wave-lengths, depends upon the nature of the surface as well as upon the temperature of the body.

By Prévost's theory of exchanges, bodies in temperature equilibrium with their surroundings emit radiation of the same character and intensity as that which they absorb. Lampblack, for instance, possesses the power of absorbing nearly all the radiation which falls upon it, and retains this power as its temperature is raised. Consequently, it must emit radiation of nearly all wave-lengths, and at a given temperature will emit more radiation than a body which possesses the power of absorbing radiation in lesser degree. A body having the power to absorb radiation of all wave-lengths completely is termed a "black body."

Owing to the equality of the radiation absorbed and emitted by any substance the character of the radiation in a uniform temperature enclosure is independent of the nature of the material forming the walls. The radiation in such an enclosure is a function of the temperature only, and is the same as that which would be emitted by a perfectly black body.

A black body is realised experimentally by having a uniform temperature enclosure with an aperture, small in comparison with the internal dimensions of the enclosure, through which the radiation may emerge. The emission of thermal radiation from, and the absorption of radiation of all wave-lengths passing into, such an enclosure is complete. Radiation from such an enclosure is known as black body, or more appropriately full radiation.

Stefan, in 1879, from a consideration of Tyndall's results on the emission of heat from glowing platinum wires, suggested that the radiation emitted by any body is proportional to the fourth power of the absolute temperature. In 1884 Boltzmann, by the application of thermodynamics to the phenomena of radiation, showed that this was the theoretical law in the case of full radiation. As use is made of the pressure exerted by radiation in Boltzmann's treatment of the subject, we shall first deduce an expression for the pressure of radiation by a method due to Larmor.

122. Larmor's Theorem.*—Consider a wave train advancing in the negative direction along the x axis with velocity c, the displacement at any time t being given by:

$$y = a \cos k(x + ct),$$

where a and k are constants.

Suppose this wave train to fall normally upon a perfect reflector advancing in the opposite direction with uniform velocity u so that its position at any time t is given by

$$x = ut.$$

There will be a reflected wave train in which the displacement is:

$$y' = a' \cos k'(x - ct).$$

The disturbance does not travel into the reflector and must therefore be annulled at this surface. Hence for $x = ut$ we have the condition:

$$y + y' = 0,$$

or

$$a \cos k(ut + ct) = - a' \cos k'(ut - ct),$$

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* Larmor, *Encyclopædia Britannica*, **22**, 787 (1911).

and this equation must be satisfied for all values of t. This condition is fulfilled if

$$a = -a'$$

and

$$k(u + c) = k'(c - u). \quad . \quad . \quad . \quad . \quad (268)$$

If λ and λ' are the wave-lengths of the incident and reflected beams respectively:

$$\lambda = \frac{2\pi}{k} \quad \text{and} \quad \lambda' = \frac{2\pi}{k'},$$

and therefore

$$\frac{\lambda'}{\lambda} = \frac{k}{k'} = \frac{c - u}{c + u}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (269)$$

from equation (268). Hence by reflection at the moving mirror the wave-length is shortened in the ratio $\frac{c - u}{c + u}$.

In a train of simple harmonic waves such as we are considering the energy is half kinetic and half potential. The kinetic energy per unit volume is obtained by integration of the expression $\frac{1}{2}\rho\left(\frac{dy}{dt}\right)^2$, ρ representing the density, whence it follows that the energy per unit volume is proportional to $\frac{1}{\lambda^2}$. If the energy per unit volume of the incident train is E, and of the reflected train E', we have:

$$\frac{E}{E'} = \frac{\lambda'^2}{\lambda^2} = \left\{\frac{c - u}{c + u}\right\}^2. \quad . \quad . \quad . \quad . \quad . \quad (270)$$

In unit time a length $(c + u)$ of the incident train moves up to the reflector, and a length $(c - u)$ is reflected. Hence the energy moving up in unit time is $(c + u)E$, and that moving away $(c - u)E'$, or the energy moving away is greater than that moving up in the ratio $\frac{c - u}{c + u} \cdot \frac{E'}{E}$, or $\frac{c + u}{c - u}$, by equation (270).

This increase in energy can only come from the work done by the mirror in advancing against the pressure p exerted by the radiation. The work done by this pressure in unit time is pu, and hence the energy moving away from the moving reflector is greater than that moving up in the ratio $\frac{(c + u)E + pu}{(c + u)E}$.

Hence

$$\frac{(c+u)E+pu}{(c+u)E}=\frac{c+u}{c-u},$$

or

$$p=2\frac{c+u}{c-u}\cdot E. \quad . \quad . \quad . \quad . \quad . \quad . \quad (271)$$

But from equation (270):

$$\frac{E+E'}{E}=\frac{(c+u)^2+(c-u)^2}{(c-u)^2},$$

$$\cdot=2\cdot\frac{c^2+u^2}{(c-u)^2},$$

or

$$E=\frac{(E+E')(c-u)^2}{2(c^2+u^2)}.$$

Substituting this value of E in equation (271) we have:

$$p=\frac{c^2-u^2}{c^2+u^2}\cdot(E+E').$$

When u is zero this equation becomes simply:

$$p=E+E',$$

or the pressure exerted on a stationary reflector is equal to the total energy density of the incident and reflected wave trains.

123. The Stefan-Boltzmann Law.—Suppose we have isotropic radiation passing through a small area da drawn anywhere in a uniform temperature enclosure. Limiting our attention for the time being to the rays incident upon da at an angle θ with the normal, the amount of radiation passing through the area in this direction is proportional to $da \cos \theta$. Also the amount of radiation propagated into a small solid angle $d\omega$ is proportional to $d\omega$. Further, the radiation passing through any area is obviously proportional to the time. Combining these results we have the amount of radiant energy propagated through the area da into the solid angle $d\omega$ in time dt given as:

$$K da \cos \theta d\omega dt, \quad . \quad . \quad . \quad . \quad . \quad . \quad (272)$$

where K is a constant known as the intensity of the radiation.

If we suppose *da* to be situated at the centre of a hemisphere of radius *r*, the total amount of energy passing downwards through the area is obtained by summing all over the hemisphere. That is, the total radiant energy passing through *da* in time *dt* is:

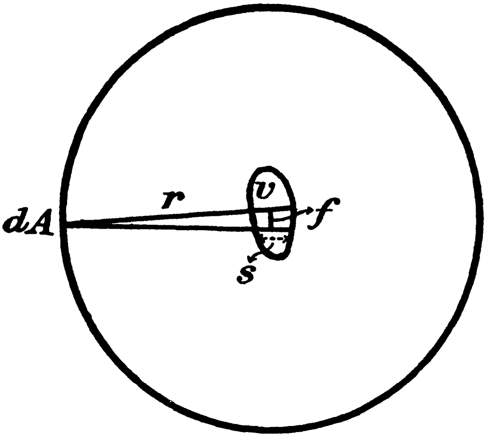

FIG. 45.

$$\int_0^{\frac{\pi}{2}} 2\pi K da dt \cos\theta \sin\theta d\theta = \pi K da dt. \quad . \quad . \quad (273)$$

As the radiation in a uniform temperature enclosure is full radiation, expression (273) must be the same as the amount of energy emitted from an area *da* of a full radiator or "black body" in time *dt*. Hence πK is the energy emitted by unit area of a black body in unit time, *i.e.* the emissive power of a black body.

Now consider a small volume *v* inside an enclosure (Fig. 45). From some point inside *v* draw a sphere of radius *r* which is large in comparison with the linear dimensions of *v*. Any radiation passing through the volume *v* must come from some point on the spherical surface. Consider the radiation which passes through the volume *v* from a small area *da* whose linear dimensions are small composed with those of *v*. The solid angle subtended at *da* by the volume *v* may be divided into a large number of infinitesimal cones, one of which is shown in the figure. If this cone has a cross-section *f* at distance *r* from the spherical surface the solid angle is given by:

$$d\omega = \frac{f}{r^2}.$$

If s is the length of the infinitesimal cone cut off by the volume v a ray will take time $\frac{s}{c}$ to travel through v, c being the velocity of light. Hence in equation (27~~4~~2), putting $dt = \frac{s}{c}$, $d\omega = \frac{f}{r^2}$, and $\cos\theta = 1$, since the linear dimensions of v are small compared with r, we obtain the amount of radiation originating from da and contained within the infinitesimal cone cut off by v as:

$$Kda\frac{f}{r^2}\cdot\frac{s}{c}.$$

Summing over the whole solid angle subtended by v at da we obtain:

$$K\frac{da}{cr^2}\Sigma f\,.\,s = K\frac{da}{cr^2}v,$$

as the total energy originating from da and contained in the volume v.

In order to obtain the total energy contained in v at any instant this last expression has to be integrated over the whole sphere. This gives the energy as:

$$4\pi\frac{K}{c}v,$$

and therefore the energy density is given by:

$$E = \frac{4\pi}{c}K,$$

and the emissive power of a black body by the equation:

$$\pi K = \tfrac{1}{4}Ec. \qquad (274)$$

In order to find the pressure exerted on a surface in the uniform temperature enclosure let us suppose that instead of the volume v we have unit area of a perfectly absorbing surface at the centre of the sphere. We will calculate the pressure on one side of this only. The amount of radiation, from an annulus of width $d\theta$ on the sphere, which arrives in unit time on the unit area, is $2\pi K\cos\theta\sin\theta\,d\theta$, and since, if this radiation were uninterrupted on its path, it would travel a distance c, the corresponding energy density is $\frac{2\pi K}{c}\cos\theta\sin\theta\,d\theta$. The normal pressure this produces is obtained by multiplication by cos θ, as the radiation approaches the unit area at θ to the normal. Hence the total pressure due to the incident radiation is given by

$$\frac{2\pi K}{c}\int_0^{\frac{\pi}{2}}\cos^2\theta\sin\theta d\theta$$

$$=\frac{2\pi K}{3c}.$$

Since the radiation moving away from the unit area considered is exactly the same as that moving up, the reaction will produce the same pressure as that due to the incident radiation, the total pressure, p, therefore being given by:

$$p=\frac{4\pi K}{3c},$$

or from equation (274)

$$p=\frac{E}{3}.$$

Suppose we have a cylinder fitted with a piston all the walls being perfectly reflecting. If this cylinder contains a small piece of matter, of negligible thermal capacity, at the temperature T to act as vehicle for the transfer of heat from outside into radiant energy in the cylinder, the radiation in the enclosure will be full radiation corresponding to the same temperature. As the walls are perfectly reflecting no heat exchange can take place between them and the radiation.

Denoting the energy density of the radiation within the cylinder by E and the volume of the enclosure by v, the total energy of the radiation is vE. Now suppose that the volume is increased by the small amount dv heat of amount δq flowing into the cylinder at the same time, and being utilised in doing external work and in changing the energy content of the cylinder. Then:

$$\delta q=d(vE)+pdv,$$

or substituting $\frac{E}{3}$ for p,

$$\delta q=d(vE)+\frac{E}{3}dv. \quad \ldots \quad (275)$$

The change of entropy in the process is given by:

$$dS = \frac{v}{T}dE + \frac{4}{3}\cdot\frac{E}{T}dv,$$

and this must be a perfect differential. Hence

$$\frac{d}{dv}\left(\frac{v}{T}\right) = \frac{d}{dE}\left(\frac{4}{3}\cdot\frac{E}{T}\right),$$

or

$$\frac{dE}{E} = 4\cdot\frac{dT}{T}.$$

Integrating this expression, we have:

$$E = aT^4,$$

where a is a constant. Thus the energy density of full radiation is proportional to the fourth power of the absolute temperature. This is the Stefan-Boltzmann law.

Substituting this value of E in equation (274) we have:

$$\begin{aligned} \pi K &= \frac{1}{4}\,acT^4 \\ &= \sigma T^4, \qquad (276) \end{aligned}$$

where σ is the Stefan-Boltzmann constant. Recently Birge,* from a consideration of all the available data on the determination of this constant, has suggested $5\cdot735 \times 10^{-5}$ erg cm.$^{-2}$ deg.$^{-4}$ sec.$^{-1}$ as its most probable value. This is in complete agreement with the value found by the author by a method which ensured black body conditions in both radiator and receiver.†

124. Full Radiation in Adiabatic Change.—Suppose we have an enclosure, whose walls reflect perfectly but diffusely, filled with full radiation at the temperature T_1. Let the enclosure expand adiabatically by a small amount so that the energy density falls to that corresponding to a temperature T_2. During this expansion the radiation will remain isotropic, because the walls reflect diffusely, but the new distribution of energy among the different wave-lengths might conceivably be different from that of full radiation of temperature T_2. If this is so the introduction into the enclosure of a small piece of matter of negligible thermal capacity will bring the radiation back to full radiation at the temperature T_2 by an irreversible process involving an increase in entropy. Now, keeping the matter in the cylinder compress the radiation adiabatically until it occupies the same volume as initially. If the matter is withdrawn from the enclosure the system will have returned to its initial state, and the work done in the expansion by the radiation must be the same as that done on the radiation in the compression, for they both depend upon the energy density. The net result of the whole process is an increase in entropy without heat having entered from outside or the performance of work. This is contrary to the second law of thermodynamics. Hence full radiation in adiabatic change must remain full radiation.

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* Birge, *Phys. Rev. Supplement*, **1**, 1 (1929).

† Hoare, *Phil. Mag.*, **28**, 828 (1928).

In adiabatic changes $\delta q = 0$, and therefore from equation (275) we have for an adiabatic expansion of radiation:

$$0 = d(vE) + \frac{E}{3}dv,$$

or

$$\frac{4}{3}\frac{dv}{v} = -\frac{dE}{E},$$

which on integration becomes:

$$Ev^{\frac{4}{3}} = E'v'^{\frac{4}{3}}, \quad . \quad . \quad . \quad . \quad . \quad (277)$$

where E' is the energy density in the volume v'. By equation (276) the energy density of full radiation is proportional to the fourth power of the absolute temperature, and therefore the last equation can be transformed to:

$$vT^3 = v'T'^3. \quad . \quad . \quad . \quad . \quad . \quad (278)$$

125. Wien's Law.—Let us consider the radiation enclosed in a spherical cavity whose walls reflect perfectly but diffusely. If the boundary of the enclosure is steadily expanding with a very small velocity u, the radiation will undergo a reversible adiabatic expansion, and in addition there will be a change in the wave-length of the radiation at each reflection from the moving walls. By equation (269) the wave-length is increased in the ratio $\frac{c+u}{c-u}$, or approximately $1 + \frac{2u}{c}$ for each reflection, if the reflecting surface is receding from radiation which is incident normally. If a ray is incident at an angle α it is the resolved part of the velocity u along the direction in which the ray is travelling, which is effective in changing the wave-length. Hence the new wave-length after oblique incidence, at an angle α with the normal, is given by:

$$\lambda' = \left(1 + \frac{2u}{c}\cos\alpha\right)\lambda.$$

Suppose a narrow beam of rays to be incident on the boundary of the spherical enclosure at the point *B*, Fig. 46, making an angle α with the radius at this point. As the walls reflect diffusely the reflected rays will not make the same angle with the radius as the incident rays. Let us limit our attention to a single ray leaving at an angle β.

If the ray starts from the point *A* at time $t = 0$ and s_1, s_2, $s_3, \ldots, s_n$ are the lengths of the chords over which it travels between successive reflections in unit time, we have:

$$c = s_1 + s_2 + s_3 + \ldots + s_n, \quad . \quad . \quad . \quad (279)$$

where c is the velocity of light. The cosines of the angles of incidence are given by:

$$\cos\alpha = \frac{s_1}{2r}, \quad \cos\beta = \frac{s_2}{2r}, \text{ etc.,}$$

and hence after the first reflection the wave-length of the radiation is given by:

$$\lambda' = \left(1 + \frac{u}{c}\frac{s_1}{r}\right)\lambda,$$

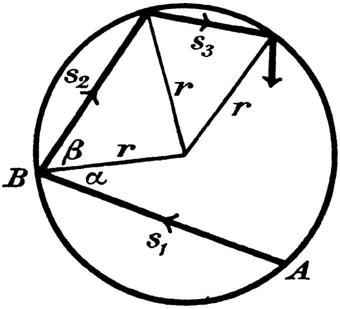

FIG. 46.

and after n reflections by:

$$\lambda' = \left(1 + \frac{u}{c}\frac{s_1}{r}\right)\left(1 + \frac{u}{c}\frac{s_2}{r}\right)\ldots\left(1 + \frac{u}{c}\frac{s_n}{r}\right)\lambda,$$

which on expansion and neglect of all powers of $\frac{u}{c}$ higher than the first becomes:

$$\lambda' = \left\{1 + \frac{u}{cr}(s_1 + s_2 + s_3 + \ldots + s_n)\right\}\lambda,$$

$$= \left(1 + \frac{u}{r}\right)\lambda,$$

by equation (279). Hence the change of wave-length in unit time, $(\lambda' - \lambda)$, is given by:

$$\frac{\lambda' - \lambda}{1} = \frac{d\lambda}{dt} = \frac{u}{r}\lambda,$$

or substituting $\frac{dr}{dt}$ for u:

$$\frac{d\lambda}{dt} = \frac{dr}{dt} \cdot \frac{\lambda}{r},$$

which on integration becomes:

$$\frac{\lambda}{r} = \frac{\lambda'}{r'}, \quad \ldots \ldots \quad (280)$$

where λ and λ' are the wave-lengths of the particular ray we are considering corresponding to radii r and r' respectively. If we consider a ray whose wave-length is very near to λ, say $\lambda + d\lambda$, we shall have:

$$\frac{\lambda + d\lambda}{r} = \frac{\lambda' + d\lambda'}{r'},$$

and therefore:

$$\frac{d\lambda}{r} = \frac{d\lambda'}{r'}. \quad \ldots \ldots \quad (281)$$

As we are considering radiation in a spherical enclosure equations (277) and (278) may be written:

$$Er^4 = E'r'^4, \quad \ldots \ldots \quad (282)$$

and

$$Tr = T'r'. \quad \ldots \ldots \quad (283)$$

Instead of considering the energy density of all the radiation we shall now limit our attention to that of the radiation lying within the narrow range of wave-length between λ and $\lambda + d\lambda$. Denoting the energy density of full radiation within this range by $E_\lambda d\lambda$, equation (282) becomes:

$$E_\lambda d\lambda r^4 = E'_{\lambda'} d\lambda' r'^4,$$

and using equations (281) and (283) this reduces to:

$$\frac{E_\lambda}{T^5} = \frac{E'_{\lambda'}}{T'^5}. \qquad (284)$$

Similarly, combining equations (280) and (283), we have:

$$\lambda T = \lambda' T'. \qquad (285)$$

If now for a given temperature the values of $\frac{E_\lambda}{T^5}$ be plotted as ordinates against those of λT as abscissæ, the resulting curve will be the same for all temperatures by virtue of equations (284) and (285). Consequently the energy density of the radiation of wave-length λ is given by:

$$\frac{E_\lambda}{T^5} = f(\lambda T),$$

or

$$E_\lambda = \frac{1}{\lambda^5} F(\lambda T), \qquad (286)$$

where f and F are functions of the product λT about which thermodynamics can give no further information. Equation (286) is Wien's general law for the distribution of energy in the spectrum of a black body.

If the distribution of energy in the spectrum is determined for any temperature T_1 and a curve showing the variation of E_λ with λ is drawn, the curve for any other temperature T_2 can be obtained by increasing E_λ in the ratio $\frac{T_2^5}{T_1^5}$ and decreasing the corresponding value of λ in the ratio $\frac{T_1}{T_2}$. It will be seen that this transformation changes the area under the curve proportionally to T^4, which agrees with the Stefan-Boltzmann law, the area bounded by the curve and the axis of λ being the total energy density.

If the curve given by equation (286) has a maximum value of E_λ at a wave-length λ_m, we must have:

$$\lambda_m T = \text{constant}. \qquad (287)$$

Thus the maximum energy density corresponds to a shorter and shorter wave-length as the temperature rises. This is ***Wien's Displacement Law.***

126. Modes of Vibration of an Elastic Solid.—Before we can determine the form of the function F in equation (286), it will be necessary to consider the number of ways in which the hypothetical medium transmitting electromagnetic disturbances is able to vibrate. Actually we shall consider the analogous problem of the modes of vibration of an elastic solid.

Suppose we have an elastic solid in the form of a rectangular block, the lengths of the sides being p, q, r, and that this block contains stationary elastic vibrations which are travelling in all directions. If the direction cosines of any wave front are l, m, n, the wave after reflection will travel in some one of the eight directions whose direction cosines are $\pm l$, $\pm m$, $\pm n$. In order that the waves may be stationary the distance traversed between two successive reflections must be some multiple of $\frac{\lambda}{2}$, λ being the wave-length of this particular vibration. We must have, therefore, that:

$$lp = n_1 \frac{\lambda}{2}, \quad mq = n_2 \frac{\lambda}{2}, \quad nr = n_3 \frac{\lambda}{2},$$

where n_1, n_2, and n_1 are integers.

Now the sum of the squares of the direction cosines is equal to unity. That is:

$$l^2 + m^2 + n^2 = 1,$$

and hence by substitution from the previous equations:

$$\frac{n_1^2}{p^2} + \frac{n_2^2}{q^2} + \frac{n_3^2}{r^2} = \frac{4}{\lambda^2}. \quad . \quad . \quad . \quad . \quad (288)$$

To every numerical triplet, n_1, n_2, n_3, there corresponds a characteristic vibration of definite wave-length and direction. Conversely only those vibrations are possible for which the values of λ satisfy equation (288) for integral values of n_1, n_2, n_3.

If the values of n_1, n_2, n_3 are plotted on three rectangular axes a simple spatial point lattice will result in which each point determines a stationary vibration of definite wave-length and direction. These points occur at the rate of one per unit volume of the ellipsoid given by equation (288), provided that the volume considered is large in comparison with the unit of length.

Considering an arbitrary range of wave-length from λ to $\lambda + d\lambda$ the number of modes of vibration with wave-lengths within this range is given by the volume of the shell bounded by two concentric ellipsoids. From the nature of the problem it is obvious that we are concerned only with the points represented by positive integers, and therefore with only one octant of the total ellipsoidal shell. Hence, as the total volume of the ellipsoid is $\frac{4}{3}\pi\frac{8pqr}{\lambda^3}$, the number of modes of vibration we are seeking is $4\pi pqr\frac{d\lambda}{\lambda^4}$, or $4\pi v\frac{d\lambda}{\lambda^4}$, where v is written for pqr, the volume of the elastic solid. Hence the number of modes of vibration with wave-lengths within the range λ to $\lambda+d\lambda$ is $\frac{4\pi}{\lambda^4}\cdot d\lambda$ per unit volume.

127. The Rayleigh-Jeans Equation for the Distribution of Energy in the Spectrum of a Black Body.

—In the case of vibrations in the ether there are two independent sets of transverse vibration corresponding to the two planes of polarisation. With each of these sets is associated the number of vibrations $\frac{4\pi}{\lambda^4}d\lambda$, so the total number of degrees of freedom in unit volume is $\frac{8\pi}{\lambda^4}d\lambda$.

From the principle of the equipartition of energy we have seen, Section 81, that the kinetic energy associated with each degree of freedom is $\frac{1}{2}kT$. In a wave motion the energy is half kinetic and half potential, so the total energy associated with each degree of freedom is kT.

Consequently the total energy in unit volume of radiation for the range of wave-length λ to $\lambda+d\lambda$ is given by:

$$E_\lambda d\lambda = \frac{8\pi}{\lambda^4}d\lambda\,.\,kT,$$

$$= \frac{8\pi kT}{\lambda^4}\cdot d\lambda. \quad . \quad . \quad . \quad . \quad . \quad . \quad (289)$$

This is the Rayleigh-Jeans equation for the distribution of energy in the spectrum. The equation obeys Wien's general law and fits the experimental results for long wave-lengths. For short waves, however, it fails for the value of E_λ would, according to this equation, rise indefinitely with decreasing wave-length, and for any finite value of T the total energy density would be infinity. The only value of T for which the total energy density would be finite is zero, and thus according to classical dynamics all the energy of matter would be dissipated away into radiation in the ether.

128. Planck's Equation.—The failure of classical dynamics to give a satisfactory equation for the distribution of energy in the spectrum of a black body led Planck* to investigate the problem in an entirely new manner. The principle of equipartition of energy assumes an interchange of energy without any lower limit to the amount of energy transferable. Planck discarded this principle of continuity in energy interchanges, assuming instead a definite lower limit to the amount of energy transferable, and that all interchanges took place in multiples of this unit. The unit of energy is a function of the frequency of the radiation itself, being in fact a constant multiplied by the frequency. That is, if ϵ is the unit of energy:

$$\epsilon = h\nu,$$

where h is Planck's constant and ν the frequency of the radiation. The quantity ϵ is the quantum of energy.

In the original deduction of his law for the distribution of energy in the spectrum Planck supposed the exchange of energy between matter and ether to be brought about by the intermediacy of particles in which electrical oscillations can take place; these particles he called resonators, and assumed that they could vibrate only with a given natural frequency. As the analysis is very complex we shall not follow Planck's original method, but a simpler deduction due to Jeans.

From considerations of the distribution of energy amongst the various members of a system containing a large number of similar parts or components, each having one degree of freedom and performing simple harmonic vibrations, it can be shown† that the most probable distribution is that in which the number of members having energy between the limits E and $E + dE$ is equal to:

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* Planck, *Ann. d. Phys.*, 4, 556 (1901). See also Rice, *Introduction to Statistical Mechanics*, p. 130.

† Jeans, *Dynamical Theory of Gases*, 2nd Edition, p. 404.

$$Be^{-\frac{E}{kT}}dE, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (290)$$

where B is a constant, k and T having their usual significance.

Now consider an amount of energy ϵ. The numbers of units having energy round about o, ϵ, 2ϵ, etc., will, by equation (290), be in the ratio:

$$1 : e^{-\frac{\epsilon}{kT}} : e^{-\frac{2\epsilon}{kT}} : e^{-\frac{3\epsilon}{kT}} : \ldots,$$

so that if N have zero energy, the numbers having energies ϵ, 2ϵ, 3ϵ, . . . will be $Ne^{-\frac{\epsilon}{kT}}$, $Ne^{-\frac{2\epsilon}{kT}}$, $Ne^{-\frac{3\epsilon}{kT}}$, etc. If M is the total number of members in the system under consideration, and each has associated with it energy of amount zero or some multiple of ϵ, we must have:

$$\begin{aligned} M &= N\left(1 + e^{-\frac{\epsilon}{kT}} + e^{-\frac{2\epsilon}{kT}} + e^{-\frac{3\epsilon}{kT}} + \ldots\right), \\ &= \frac{N}{1 - e^{-\frac{\epsilon}{kT}}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (291) \end{aligned}$$

The total energy of all the members is:

$$\begin{aligned} &\epsilon Ne^{-\frac{\epsilon}{kT}} + 2\epsilon Ne^{-\frac{2\epsilon}{kT}} + 3\epsilon Ne^{-\frac{3\epsilon}{kT}} + \ldots, \\ &\qquad = \epsilon Ne^{-\frac{\epsilon}{kT}}\left\{1 + 2e^{-\frac{\epsilon}{kT}} + 3e^{-\frac{2\epsilon}{kT}} + \ldots\right\}, \\ &\qquad = \frac{N\epsilon e^{-\frac{\epsilon}{kT}}}{\left(1 - e^{-\frac{\epsilon}{kT}}\right)^2}, \\ &\qquad = \frac{M\epsilon}{e^{\frac{\epsilon}{kT}} - 1}, \end{aligned}$$

by equation (291).

Hence the average energy to be associated with each degree of freedom is:

$$\frac{\epsilon}{e^{\frac{\epsilon}{kT}} - 1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (292)$$

If we assume that the quantity of energy ϵ is infinitely small, the mean energy of a vibration is obtained by finding the limit to which expression (292) tends as ϵ approaches zero. Expanding the expression it will be seen to be of the form:

$$\frac{\epsilon}{\frac{\epsilon}{kT}+\frac{1}{2}\left(\frac{\epsilon}{kT}\right)^2+\frac{1}{6}\left(\frac{\epsilon}{kT}\right)^3+\ldots},$$

which tends to the value kT as ϵ approaches zero. Thus the difference between the mean energy given by expression (292) and the equipartition value kT arises from the assumption that energy cannot be subdivided without limit.

Replacing the energy ϵ by $h\nu$ in accordance with the principles of the quantum theory, we obtain the energy to be associated with each degree of freedom as:

$$\frac{h\nu}{e^{\frac{h\nu}{kT}}-1}. \quad \ldots \ldots \quad (293)$$

We have already seen that the number of vibrations in unit volume of ether whose wave-lengths lie between λ and $\lambda + d\lambda$ is $\frac{8\pi}{\lambda^4} \cdot d\lambda$. As an amount of energy given by expression (293) has to be associated with each of these vibrations the equation for the distribution of energy in the spectrum, after substituting $\frac{c}{\lambda}$ for ν, becomes:

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5\left(e^{\frac{hc}{k\lambda T}}-1\right)} \cdot d\lambda,$$

or

$$E_\lambda = \frac{c_1}{\lambda^5\left(e^{\frac{c_2}{\lambda T}}-1\right)}. \quad \ldots \quad (294)$$

This is Planck's equation; the agreement between this theoretical equation and the experimental results is very close.*

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* See *La Théorie du rayonnement et les Quanta*, Langevin and de Broglie.

129. Examination of Planck's Equation.—From the form of equation (294) it will be seen that it satisfies Wien's general law, and also the displacement law. For large values of λ the equation reduces to the Rayleigh-Jeans equation, as would be expected.

In Fig. 47 the full line shows the distribution of energy in the spectrum of a black body as given by Planck's equation for $T = 1{,}000^\circ$. The broken line shows the locus of maxima for different temperatures.

The wave-length λ_m corresponding to maximum energy density is obtained by differentiating equation (294) with respect to λ and equating to zero. Thus we have:

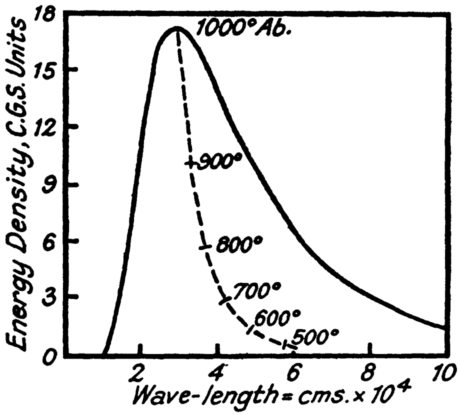

FIG. 47.

Planck's Equation.

$$e^{-x} + \frac{x}{5} - 1 = 0,$$

where x is written for $\frac{c_2}{\lambda_m T}$. The solution of this equation is:

$$x = 4{\cdot}9651,$$

and therefore

$$\lambda_m T = \frac{c_2}{4{\cdot}9651}.$$

The experimental value for c_2* is 1·432 cm. deg., and hence

$$\lambda_m T = 0{\cdot}2884 \text{ cm. deg.}$$

The total energy density of full radiation is obtained by integrating Planck's equation over all values of λ. Thus we have:

$$E = \int_0^\infty E_\lambda d\lambda = \int_0^\infty \frac{c_1}{\lambda_5\left(e^{\frac{c_2}{\lambda T}} - 1\right)} \,.\, d\lambda.$$

This integral can be evaluated if we write:

$$\lambda = \frac{1}{y},$$

so that

$$d\lambda = -\frac{dy}{y^2}.$$

Making this substitution the equation becomes:

$$E = c_1 \int_0^\infty y^3 e^{-\frac{c_2}{T}y}\left(1 - e^{-\frac{c_2}{T}y}\right)^{-1} dy,$$

$$= c_1 \int_0^\infty y^3 e^{-\frac{c_2}{T}y}\left(1 + c^{-\frac{c_2}{T}y} + e^{-\frac{2c_2}{T}y} + \ldots\right) dy.$$

This may be integrated term by term when we have:

$$E = c_1 \,.\, 6 \,.\, \frac{T^4}{c_2{}^4}\left(\frac{1}{1^4} + \frac{1}{2^4} + \frac{1}{3^4} + \ldots\right),$$

$$= 6 \,.\, c_1 \,.\, \frac{T^4}{c_2{}^4}\frac{\pi^4}{90},$$

$$= \frac{8}{15} \cdot \frac{\pi^5 k^4}{h^3 c^3} \cdot T^4,$$

on substitution for c_1 and c_2.

* See *Dictionary of Applied Physics*, **4**, Art. Radiation, W. W. Coblentz.

By our previous results:

$$E = \frac{4\pi}{c} . K = \frac{4}{c} . \sigma T^4,$$

and therefore

$$\sigma = \frac{2}{15} \cdot \frac{\pi^5 k^4}{h^3 c^2}.$$

Consequently determinations of the constants σ and $c_2 \left(= \frac{hc}{k} \right)$ enable the values of the constants h and k to be evaluated from the equations:

$$\left. \begin{aligned} h &= \frac{15\sigma c_2^4}{2\pi^5 c^2} \\ \text{and} \quad k &= \frac{15\sigma c_2^3}{2\pi^5 c} \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (295)$$

Taking the experimental values as:

$$\begin{aligned} \sigma &= 5 \cdot 735 \times 10^{-5} \text{ erg cm.}^{-2} \text{ deg.}^{-4} \text{ sec.}^{-1}, \\ c_2 &= 1 \cdot 432 \text{ cm. deg.}, \\ c &= 3 \times 10^{10} \text{ cm. sec.}^{-1}, \end{aligned}$$

the values of h and k given by equations (295) are:

$$\begin{aligned} h &= 6 \cdot 568 \times 10^{-27} \text{ erg sec.} \\ k &= 1 \cdot 376 \times 10^{-16} \text{ erg deg.}^{-1}. \end{aligned}$$

These are higher than the values given by Birge,* namely $6 \cdot 547 \times 10^{-27}$ erg sec. and $1 \cdot 3708 \times 10^{-16}$ erg deg.$^{-1}$ respectively. As the quantity c_2 occurs to the fourth and third powers in equations (295), any small error in the determination of this constant will have a relatively large effect on the values of h and k. If c_2 is taken as $1 \cdot 431$ cm. deg., the values of h and k obtained from equations (295) are in very good agreement with those given by Birge.

Having determined the value of k the number of molecules in a gram molecule, N, can be deduced for

$$R = Nk$$

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* Birge, *loc. cit.*

Thus, taking the values:

$$\boldsymbol{k} = 1 \cdot 376 \times 10^{-16} \text{ erg deg.}^{-1},$$
$$\boldsymbol{R} = 1 \cdot 985 \text{ calories deg.}^{-1},$$

we find the value of $\boldsymbol{N}$ to be given as:

$$\boldsymbol{N} = 6 \cdot 038 \times 10^{23}.$$

CHAPTER XIII

ON THE VARIATION OF SPECIFIC HEAT WITH TEMPERATURE

130. The Law of Dulong and Petit.—The first attempt to obtain a general law connecting specific heat with other properties of a body was made in 1819 by Dulong and Petit, who, from a consideration of the experimental data then available, came to the conclusion that the product of atomic weight and specific heat of a substance is a constant, approximately 6·4. This law can be deduced, using the principle of the equipartition of energy, in the following manner.

In a solid the constituent atoms may be regarded as being free to vibrate in three mutually perpendicular directions. Assuming the vibrations to be simple harmonic the total mean energy associated with any atom will be half kinetic and half potential. Now the principle of equipartition of energy is considered to hold equally well for all states of matter, so the total energy of each degree of freedom will be kT, and that of one atom $3kT$. If in one gram of the substance under consideration there are N atoms, the total energy of this mass is given by:

$$E = 3NkT.$$

As has already been shown, the specific heat at constant volume is $\left(\frac{dE}{dT}\right)_v$, and therefore

$$C_v = 3Nk.$$

Multiplying each side of this equation by a, the atomic weight of the substance, we have:

$$aC_v = 3aNk.$$

It is generally agreed that in solid elements—the metals—the gram atom and the gram molecule are identical, so aN is the number of molecules in a gram molecule, i.e. Avogadro's number

N. Hence, since $Nk = R$, the atomic heat of a solid should be given by:

$$C_v = 3R,$$

where C_v now represents the specific heat per gram atom or the atomic heat. Substituting the value 1·985 calories per degree for R:

$$C_v = 5{\cdot}955 \text{ calories per degree.}$$

Thus according to the principle of the equipartition of energy the atomic heat of monatomic solids should be a constant, the same for all substances, and independent of the temperature. The following table* gives the values of the atomic heats for various elements at 273·1° and 50° K.

TABLE XIV.

Element.	Atomic Weight.	Atomic Heat at 0° C. Calories Degree−1.	Atomic Heat at − 223·1° C. Calories Degree−1.
Ag	107·88	6·02	2·70
Al	27·1	5·70	0·90
C (diamond) ..	12·00	1·20	0·00
Ca	40·09	6·18	2·74
Cd	112·40	6·19	3·68
Cu	63·57	5·78	1·44
Fe	55·85	5·84	0·90
Hg	200·0	6·69	4·99
K	39·10	7·07	5·16
Mg	24·32	6·02	1·50
Na	23·00	6·73	3·20
Pb	207·10	6·30	5·17
Si	28·3	4·52	0·46
Sn (white) ..	119·0	6·40	3·67
Tl	204·0	6·33	4·95
W	184·0	6·02	1·44
Zn	65·37	6·01	2·45

It will be observed that although the values of the atomic heat at 0° C. fluctuate to some extent, they are generally not far from a mean value of 6·4, but at the lower temperature they fall considerably below this value. The variation of the atomic heat with temperature makes it at once apparent that the law of Dulong and Petit can only be regarded as an approximation. The apparent deviation at 0° C. from the theoretical value of 5·955 for the atomic heat arises from the fact that the above tabulated values refer to the atomic heat at constant pressure, which is, of course, greater than that at constant volume.

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* Values taken from *International Critical Constants*, vol. 5.

The case of carbon is of special interest, as it is one of the notable exceptions to the law of Dulong and Petit at ordinary temperatures. In the following table are given the atomic heats of carbon (diamond) as given by Magnus.*

TABLE XV.

T.	C_p.	C_v.	T	C_p.	C_v.
86·5	0·03	0·03	530·0	3·631	3·614
92·0	0·03	0·03	600	3·974	3·952
205·0	0·62	0·62	650	4·176	4·149
209·0	0·66	0·66	700	4·360	4·329
220·0	0·72	0·72	750	4·525	4·489
222·5	0·762	0·762	800	4·671	4·630
261·4	1·146	1·145	850	4·798	4·752
283·7	1·354	1·353	900	4·905	4·854
306·4	1·582	1·580	950	4·995	4·939
331·3	1·838	1·835	1,000	5·064	5·003
358·5	2·118	2·114	1,050	5·115	5·051
413·0	2·662	2·665	1,100	5·146	5·077
479·1	3·280	3·268	—	—	—

It will be noticed that the atomic heat rises from the low value 0·03 at 86·5° to 5·077 at 1,100°. This is a general tendency observed for all substances having a low atomic heat at ordinary temperatures. It appears that the atomic heat increases with rise of temperature approximating at high temperatures to the value 5·955.

131. Einstein's Equation.—The success attending the application of the quantum theory to the radiation problem led Einstein to apply the same theory to the problem of the variation of specific heat with temperature. Instead of assigning the equipartition value kT to each vibration of the atom he suggested that the average energy for a linear vibration should be that given by equation (293), namely:

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* Magnus, *Ann. der Phys.*, **70**, 303 (1923).

$$\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}.$$

Consequently the total internal energy of one gram atom of a solid, each atom of which can vibrate in three mutually perpendicular directions with a single constant frequency ν, is given by:

$$E = \frac{3Nh\nu}{e^{\frac{h\nu}{kT}} - 1}.$$

Differentiating E with respect to T, we obtain Einstein's equation for the atomic heat of a monatomic solid. Thus

$$C_v = \left(\frac{dE}{dT}\right)_v = 3Nk\left(\frac{h\nu}{kT}\right)^2 \frac{e^{\frac{h\nu}{kT}}}{\left(e^{\frac{h\nu}{kT}} - 1\right)^2},$$

$$= 3R\left(\frac{h\nu}{kT}\right)^2 \frac{e^{\frac{h\nu}{kT}}}{\left(e^{\frac{h\nu}{kT}} - 1\right)^2} \quad . \quad . \quad (296)$$

From the form of this equation it is apparent that as the temperature approaches zero so also does the atomic heat, whilst at high temperatures the value $3R$ is approached as a limit. It remains to be seen, however, if the quantitative agreement between equation (296) and the experimental results is sufficiently close. Table XVI indicates the degree of accuracy obtainable. The column headed C_v (calculated) has been obtained by choosing the experimentally determined value of C_v at $T = 306{\cdot}4^\circ$ and hence calculating ν, the frequency so obtained being used to calculate the values of C_v at other temperatures.

The general form of the curve given by Einstein's equation is shown in Fig. 48, the observations of Table XVI being indicated by the small circles.

132. The Nernst-Lindemann Equation.—The atomic heats of a large number of substances show a much more gradual decrease at very low temperatures than is demanded by equation (296). Nernst and Lindemann* proposed an empirical expression

TABLE XVI.

Atomic Heat of Carbon (Diamond).

T.	$\frac{kT}{h\nu}$.	C_v. (Observed).	C_v (Calculated).
92·0	0·0706	0·03	0·0008
220·0	0·1688	0·72	0·433
283·7	0·2179	1·353	1·267
306·4	0·2353	1·580	1·581
331·3	0·2545	1·835	1·879
479·1	0·3681	3·268	3·331
600	0·4608	3·952	4·082
800	0·6144	4·630	4·796
1,000	0·7681	5·003	5·181

for C_v which is capable of representing the experimental results with a much greater degree of accuracy than Einstein's equation. Their equation takes the form:

$$C_v = \tfrac{3}{2}R\left\{\frac{\left(\frac{h\nu}{kT}\right)^2 e^{\frac{h\nu}{kT}}}{\left(e^{\frac{h\nu}{kT}} - 1\right)^2} + \frac{\left(\frac{h\nu}{2kT}\right)^2 e^{\frac{h\nu}{2kT}}}{\left(e^{\frac{h\nu}{2kT}} - 1\right)^2}\right\} \quad . \quad . \quad (297)$$

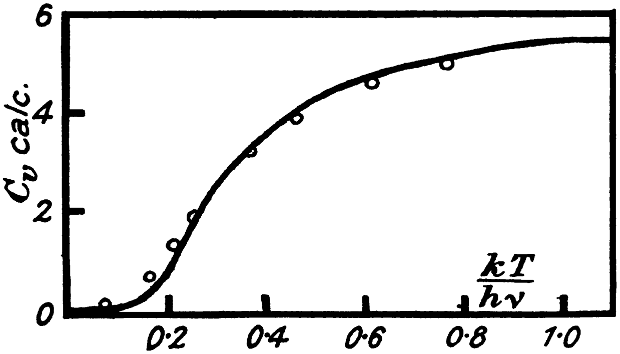

FIG. 48.

Einstein's Equation.

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* Nernst and Lindemann, *Berliner Sitzungsber.*, 494 (1911).

The introduction of the octave term has little or no theoretical justification, but the better agreement between this equation and the experimental results suggests that Einstein's equation owes its deficiencies primarily to the choice of a single fixed frequency, and that to arrive at a perfectly satisfactory expression the atom should be regarded as possessing a whole spectrum of elastic frequencies to each of which must be allotted energy of amount $\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$.

The method adopted by Nernst and Lindemann* for the derivation of C_p from the calculated values of C_v deserves special mention. As sufficient data were not available for the calculation of C_p from the thermodynamic relation, equation (57):

$$C_p = C_v + Kva^2T,$$

these experimenters, in an extensive test of their equation, adopted a different procedure. Experiment has shown that Kv is approximately constant at all temperatures, and therefore, as it only enters in a relatively small correction term, little error will be introduced by so considering it. Further, it has been shown by Grüneisen† that the specific heat at constant pressure is proportional to the coefficient of expansion, and therefore the above expression can be written:

$$C_p = C_v + BC_p^2T,$$

where B is a constant characteristic of each substance. It was also shown that the individual constant B is inversely proportional to the melting-point T_s. The above relation can then be written in the form:

$$C_p = C_v + C_p^2 \frac{T}{T_s} B_o, \quad . \quad . \quad . \quad . \quad (298)$$

where B_0 is a universal constant having the value 0·0214 deg. cal.$^{-1}$. The following table, given by Schrödinger,‡ illustrates the agreement between the ratio $\frac{C_p}{C_v}$ as calculated by equations (57) and (298) respectively.

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* Nernst and Lindemann, *Zeits. f. Electrochem.*, **17**, 817 (1911).

† Grüneisen, *Verh. d. D. Phys. Ges.*, **13**, 426 and 491 (1911).

‡ Schrödinger, *Phys. Zeit.*, **20**, 452 (1919).

TABLE XVII.

		Al.	Cu.	Ag.	Pb.	Pt.	NaCl.	KCl.
$\frac{C_p}{C_v}$	Equation (57)	1·042	1·025	1·047	1·055	1·019	1·051	1·038
	Equation (298)	1·040	1·027	1·032	1·068	1·019	1·036	1·039

In testing their equation Nernst and Lindemann calculated C_v, and from this obtained the value of C_p by one or other of the methods outlined above. This value of C_p was then directly compared with the observed value.

133. Debye's Equation.—Debye* has attacked the problem of the variation of specific heat with temperature in a manner which takes into account the various vibration frequencies which are possible for any atom.

If an atom could vibrate with all frequencies from $\nu = 0$ to $\nu = \infty$, the total number of degrees of freedom would be infinite. Since one gram atom contains N atoms each of three degrees of freedom the whole mass possesses only $3N$ degrees of freedom. Consequently Debye assumes that the whole range of frequencies is not possible, but is sharply terminated at an upper limit ν_m related to the atomic dimensions.

In an elastic solid two kinds of wave are possible, longitudinal and transverse, and since any transverse wave of given frequency and direction may be resolved into two independent components at right angles, the total number of modes of vibration of unit mass of an elastic solid whose frequencies lie between ν and $\nu + d\nu$ will not be that given in section 126, but:

$$4\pi v\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right)\nu^2 d\nu,$$

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* Debye, *Ann. d. Phys.*, **39**, 789 (1912).

where c_l and c_t are the velocities of propagation of longitudinal and transverse waves respectively, and v is the volume of the body considered.

Hence the number of modes of vibration with frequencies between zero and ν_m is given by:

$$\int_0^{\nu_m} 4\pi v\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)\nu^2 d\nu,$$

and this must be equal to $3N$. Thus we have:

$$3N = \frac{4}{3}\pi v\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)\nu_m^3. \quad . \quad . \quad . \quad . \quad (299)$$

As energy of amount $\dfrac{h\nu}{e^{\frac{h\nu}{kT}}-1}$ has to be assigned to each degree of freedom we have for the total energy of the solid:

$$E = \int_0^{\nu_m} 4\pi v\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)\frac{h\nu^3}{e^{\frac{h\nu}{kT}}-1}d\nu,$$

which by equation (299) reduces to:

$$E = \frac{9N}{\nu_m^3}\int_0^{\nu_m}\frac{h\nu^3}{e^{\frac{h\nu}{kT}}-1}d\nu.$$

Differentiating this expression with respect to T, we obtain for C_v the atomic heat at constant volume:

$$C_v = \frac{9N}{\nu_m^3}\int_0^{\nu_m}\frac{\frac{h^2\nu^4}{kT^2}\cdot e^{\frac{h\nu}{kT}}}{\left(e^{\frac{h\nu}{kT}}-1\right)^2}\cdot d\nu.$$

Making the substitutions:

$$x_m = \frac{h\nu_m}{kT},$$

$$x = \frac{h\nu}{kT},$$

$$dx = \frac{h}{kT}\cdot d\nu,$$

the last equation becomes:

$$C_v = \frac{9Nk}{x_m^3}\int_0^{x_m}\frac{x^4e^x}{(e^x-1)^2}dx,$$

$$= \frac{9R}{x_m^3}\int_0^{x_m}\frac{x^4e^x}{(e^x-1)^2}dx.$$

Integrating this equation by parts the value of C_v is finally given by:

$$C_v = 3R\left\{\frac{12}{x_m^3}\int_0^{x_m}\frac{x^3}{e^x-1}\,dx - \frac{3x_m}{e^{x_m}-1}\right\}. \quad . \quad . \quad (300)$$

This is Debye's equation.

134. Examination of Debye's Equation.—For high temperatures the value of x becomes very small and therefore as:

$$\underset{x\to 0}{\text{Limit}}\int_0^{x_m}\frac{x^3}{e^x-1}\,dx = \int_0^{x_m}x^2dx = \frac{x_m^3}{3},$$

and

$$\underset{x\to 0}{\text{Limit}}\;\frac{3x_m}{e^{x_m}-1} = 3,$$

the atomic heat approaches the value $3R$ in accordance with the law of Dulong and Petit.

The value of x at low temperatures is large, and the second term on the right-hand side of equation (300) vanishes in comparison with the first. Also we see, by comparison with section 129, that

$$\int_0^{\infty}\frac{x^3}{e^x-1}dx = \frac{\pi^4}{15}.$$

Hence the atomic heat at low temperatures is given approximately by the equation:

$$C_v = \frac{12}{5}R\pi^4\frac{T^3}{T_m{}^3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (301)$$

or at low temperatures the atomic heat is proportional to the cube of the absolute temperature. This is known as the Debye T^3 law.

From the form of equation (300) it is apparent that the bracketed term is a function of x_m only. Also, since $\frac{h\nu_m}{kT}$ must be a pure number the dimensions of $\frac{h\nu_m}{k}$ are those of temperature. Hence replacing $\frac{h\nu_m}{k}$ by T_m, a characteristic temperature associated with each substance, the bracketed term can be written as $f\left(\frac{T_m}{T}\right)$ where f is a function of the same form for all substances. The equation for the atomic heat of any substance then becomes:

$$C_v = 3Rf\left(\frac{T_m}{T}\right).$$

The evaluation and computation of the function f have been accomplished by Debye. The following table gives the values of C_v for various values of $\frac{T}{T_m}$.*

TABLE XVIII.

$\frac{T}{T_m}$.	C_v.	$\frac{T}{T_m}$.	C_v.	$\frac{T}{T_m}$.	C_v.
∞	5·955	0·8	5·515	0·20	2·198
4	5·937	0·7	5·383	0·15	1·269
3	5·919	0·6	5·193	0·10	0·4514
2	5·884	0·5	4·913	0·075	0·1953
1·5	5·824	0·4	4·437	0·050	0·0580
1·0	5·699	0·3	3·615	0·025	0·0073
0·9	5·604	0·25	2·996	0·000	0·0000

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* Values of $f\left(\frac{T_m}{T}\right)$ from Jeans, *Dynamical Theory of Gases*, 2nd Edition, p. 424.

These results are shown graphically in Fig. 49, the experimental results for aluminium, copper, and silver being indicated on the same curve.

135. Comparison with Experiment.—The three equations, (296), (297), and (300), proposed to represent the variation of atomic heat with temperature, have been tested in detail by a number of experimenters. Table XIX, page 256,* incorporating results obtained by Dewar, Nernst, and E. H. and Ezer Griffiths, indicate the agreement between the observed results and those calculated by use of the three different equations. The columns headed (E.), (N & L.) and (D.) are the atomic heats as obtained from the equations of Einstein, Nernst and Lindemann, and Debye respectively, the value of C_p having been obtained from the calculated value of C_v by one or other of the methods indicated in section 132. The values of $\frac{h\nu}{k}$ are given at the top of the columns, ν having been chosen so as to bring the calculated values of the atomic heat into coincidence with the experimental values at one temperature (about 125° K).

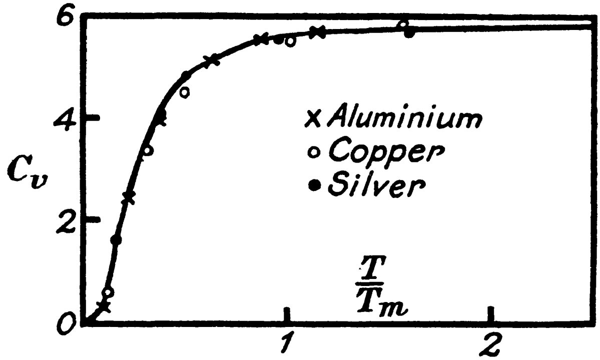

FIG. 49.

Debye's Equation.

From these results it will be seen that Debye's equation is, in general, very closely verified by experiment, and is capable of representing the variation of atomic heat with temperature with

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* E. H. Griffiths and Ezer Griffiths, *Phil. Trans. Roy. Soc.*, A, **214**, 350 (1914); also *Dict. App. Phys.*, **1**, 73 (1922).

Table XIX.

T.	C_p (observed).	C_p (E.).	C_p (N. & L.).	C_p (D.).
Aluminium		$\frac{h\nu}{k} = 292.$	$\frac{h\nu}{k} = 385.$	$\frac{h\nu_m}{k} = 385.$
35°	0·33	0·12	0·37	0·35
80	2·27	2·18	2·46	2·35
140	4·26	4·26	4·26	4·28
200	5·14	5·12	5·10	5·10
250	5·53	5·49	5·47	5·47
300	5·81	5·75	5·74	5·74
380	6·13	6·02	6·01	6·01
Copper		$\frac{h\nu}{k} = 222.$	$\frac{h\nu}{k} = 285.$	$\frac{h\nu_m}{k} = 286.$
33·4°	0·54	0·36	0·82	0·71
88	3·38	3·60	3·74	3·70
120	4·58	4·52	4·58	4·57
200	5·44	5·46	5·47	5·47
280	5·80	5·78	5·80	5·80
360	6·02	5·96	6·01	6·01
Zinc		$\frac{h\nu}{k} = 160.$	$\frac{h\nu}{k} = 210.$	$\frac{h\nu_m}{k} = 210.$
30°	0·95	0·84	1·30	1·13
80	4·09	4·33	4·33	4·33
130	5·31	5·32	5·31	5·31
200	5·78	5·76	5·77	5·77
280	6·02	6·00	6·01	6·00
360	6·21	6·19	6·19	6·19
Silver		$\frac{h\nu}{k} = 157.$	$\frac{h\nu}{k} = 207.$	$\frac{h\nu_m}{k} = 207.$
35°	1·58	1·40	1·80	1·64
85	4·42	4·56	4·53	4·53
120	5·20	5·23	5·21	5·21
200	5·84	5·73	5·78	5·78
280	6·01	6·01	6·01	6·01
360	6·16	6·16	6·16	6·15

TABLE XIX. (*continued*).

T.	C_p (observed).	C_p (E.).	C_p (N. & L.).	C_p (D.).
Cadmium ..	.. ..	$\frac{h\nu}{k} = 112.$	$\frac{h\nu}{k} = 143.$	$\frac{h\nu_m}{k} = 144.$
50°	3·46	4·02	4·10	4·10
115	5·60	5·59	5·60	5·60
160	5·87	5·85	5·86	5·86
200	5·99	5·97	5·99	5·99
360	6·39	6·33	6·34	6·34
Lead ..	.. ..	$\frac{h\nu}{k} = 68.$	$\frac{h\nu}{k} = 92.$	$\frac{h\nu_m}{k} = 94.$
23°	2·96	3·03	3·06	2·94
80	5·72	5·75	5·65	5·64
120	5·93	5·93	5·91	5·91
200	6·10	6·13	6·13	6·13
280	6·28	6·28	6·28	6·28
360	6·45	6·45	6·45	6·45
Sodium ..	.. ..	$\frac{h\nu}{k} = 119.$	$\frac{h\nu}{k} = 152.$	$\frac{h\nu_m}{k} = 152.$
50°	3·50	3·87	3·98	3·95
120	5·62	5·62	5·64	5·64
200	6·17	6·02	6·04	6·02
320	6·78	6·36	6·36	6·36
360	7·32	6·43	6·43	6·43
Iron ..	.. ..	$\frac{h\nu}{k} = 286.$	$\frac{h\nu}{k} = 376.$	$\frac{h\nu_m}{k} = 376.$
50°	0·98	0·65	1·10	0·98
140	4·28	4·28	4·29	4·29
220	5·45	5·24	5·21	5·21
300	6·03	5·62	5·61	5·61
380	6·37	5·82	5·82	5·82

greater accuracy than the equations of Einstein or Nernst and Lindemann.

Schrödinger* has made an exhaustive analysis of the experimental data and found that the same curve represents the variation of atomic heat of a large number of different substances with remarkable accuracy.

136. The Debye T^3 Law.—In the paper by Schrödinger† already quoted will be found a number of tables showing how at low temperatures the T^3 law is obeyed. The following table, giving the results for copper, is typical.

TABLE XX.

T.	C_v.	$\frac{10^2}{T} \times \sqrt[3]{C_v}$.
14·51	0·0396	2·35
15·24	0·0491	2·40
15·60	0·0506	2·37
17·17	0·0687	2·39
17·50	0·0726	2·39
18·03	0·0792	2·38
18·89	0·0930	2·40
19·58	0·1010	2·45
20·20	0·1155	2·42
20·75	0·1217	2·39
20·88	0·1247	2·40
21·50	0·1410	2·42
23·5	0·22	2·57
25·37	0·234	2·43
27·7	0·32	2·47

It is probable that the T^3 law applies to all substances at the lowest temperatures irrespective of whether the Debye law is obeyed at higher temperatures or not.

137. Extension of Theory to Crystalline Bodies.—The theory of the variation of specific heat so far developed is applicable only in the case of an isotropic body in which all the atoms are similar. Nernst and others have extended the theory to the molecular heats of polyatomic solids. According to Nernst there are two types of vibration in such a solid to be considered; first there is the vibration of the molecule as a whole, and secondly the vibrations of the atom within the molecule. These vibrations are supposed to be represented by the formulæ of Debye and Einstein respectively, the mean atomic heat C_v, i.e. molecular heat divided by the number of atoms in a molecule, in the case of a diatomic solid such as KCl, being given by an equation of the type:

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* Schrödinger, *loc. cit.*, p. 452.

† *Ibid.*, p. 498.

$$C_v = \frac{1}{2}\left\{F_1\left(\frac{h\nu_1}{kT}\right) + F_2\left(\frac{h\nu_2}{kT}\right)\right\}, \quad . \quad . \quad . \quad (302)$$

where F_1 and F_2 are the Debye and Einstein functions. In this equation ν_1 is obtained from the melting-point formula of Lindemann and ν_2 from observations upon *reststrahlen.**

Equation (302) has been generalised to apply to a crystalline body having n atoms in a molecule, the body supposed not to be isotropic. In this case the equation is:

$$C_v = \frac{1}{3n}\left\{\sum_{l=1}^{l=3} F_1\left(\frac{h\nu_l}{kT}\right) + \sum_{l=4}^{l=3n} F_2\left(\frac{h\nu_l}{kT}\right)\right\}.$$

It is found that the atomic heat of some compounds can be represented by a single Debye term as well as by either of the above equations. A useful summary of the experimental work on substances not obeying Debye's simple law will be found in Schrödinger's paper.†

138. The Determination of the Characteristic Vibration Frequency of a Solid.—There are several independent methods by which the characteristic vibration frequency used in the equations for atomic heat may be determined.

The first of these depends upon the property of selective reflection, i.e. the power to reflect radiation of particular wave-lengths more strongly than others, possessed by a number of substances. If a beam of full radiation is reflected successively from several pieces of a solid having this property the reflected radiation becomes increasingly pure, tending to consist more and more of one particular wave-length. The rays which survive after a number of such reflections are termed *reststrahlen* or residual rays. It should be noticed that the *reststrahlen* are those rays which would be most strongly absorbed on transmission. The wave-length of these rays corresponds to the natural vibration frequency of the atoms, for it is when the radiation has the same frequency as the vibrating atom that it is most strongly absorbed. Measurements of the wave-length of the *reststrahlen* thus enable the characteristic frequency to be determined. The investigation of these rays has been principally carried out by Rubens and his collaborators.*

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* See next section.

† *Loc. cit.*, p. 478.

Another method, due to Lindemann,† is based upon the assumption that at the temperature of fusion of a solid the amplitude of vibration of the atoms is approximately equal to their mean distance apart.

Thus if r is the radius of the circular vibration of an atom, the mean velocity u with which it vibrates is given by:

$$u = 2\pi r\nu,$$

where ν is the frequency as before. Consequently the total energy associated with the vibration being half kinetic and half potential it is given by:

$$mu^2 = m4\pi^2r^2\nu^2.$$

Now at its melting-point, T_s, a solid can be considered as obeying Dulong and Petit's law, the energy per atom then being $3kT_s$. Hence at this point

$$4\pi^2mr^2\nu^2 = 3kT_s,$$

or

$$\nu\propto\sqrt{\frac{T_s}{mr^2}}.$$

According to Lindemann's assumption the radius r is equal to the mean distance apart of the atoms, and hence the atomic volume v is proportional to r^3. Therefore we have:

$$\nu\propto\sqrt{\frac{T_s}{av^{\frac{2}{3}}}}$$

where a is the atomic weight.

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* *Ann. d. Phys.*, **60**, 418 (1897); **65**, 241 (1898); **69**, 576 (1899); **4**, 649, (1901); *Phil. Mag.*, **19**, 761 (1910).

† Lindemann, *Phys. Zeits.*, **11**, 609 (1910)

By comparison with experiment it is found that the constant of proportionality is $2{\cdot}80 \times 10^{12}$, so the frequency is given by:

$$\nu = 2{\cdot}80 \times 10^{12}\sqrt{\frac{T_s}{av^{\frac{2}{3}}}} \quad . \quad . \quad . \quad . \quad (303)$$

A value for ν_m, the maximum frequency of Debye's equation, can be obtained from measurements of the elastic constants. If the bulk modulus of elasticity, Poisson's ratio, and the density of an isotropic body, are denoted by K, σ, and ρ respectively, it can be shown that:

and

$$\left.\begin{aligned} c_l &= \sqrt{\frac{3K(1-\sigma)}{\rho(1+\sigma)}}, \\ c_t &= \sqrt{\frac{3K(1-2\sigma)}{2\rho(1+\sigma)}}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (304)$$

where c_l and c_t are the velocities of propagation of longitudinal and transverse elastic waves respectively. If in equation (299) we make the substitution:

$$\frac{1}{\bar{c}^3} = \frac{1}{3}\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right),$$

the maximum frequency ν_m is obviously given by:

$$\nu_m = \bar{c}\sqrt[3]{\frac{3N}{4\pi v}}. \quad . \quad . \quad . \quad . \quad . \quad (305)$$

From equations (304) above $\bar{c}$ can be written as:

$$\bar{c} = \sqrt{\frac{K}{\rho}} \cdot \psi(\sigma),$$

where $\psi(\sigma)$ is a definite function of σ, given by:

$$\psi(\sigma) = \left\{\frac{2}{3}\left(\frac{2(1+\sigma)}{3(1-2\sigma)}\right)^{\frac{3}{2}} + \frac{1}{3}\left(\frac{1+\sigma}{3(1-\sigma)}\right)^{\frac{3}{2}}\right\}^{-\frac{1}{3}}.$$

Since $v = \frac{a}{\rho}$, a being the atomic weight of the substance, we have from equation (305):

$$\nu_m = \sqrt[3]{\frac{3N}{4\pi}} \cdot \frac{K^{\frac{1}{2}}\psi(\sigma)}{a^{\frac{1}{3}}\rho^{\frac{1}{6}}} \quad . \quad . \quad . \quad . \quad . \quad (306)$$

The following table* gives the value of $T_m \left(= \frac{h\nu_m}{k}\right)$ as obtained from atomic heat data, the elastic constants, Lindemann's melting-point equation, and from observations upon *reststrahlen.*

Substance.	Value of T_m as Obtained from			
	Atomic Heat.	Elastic Constants.	Lindemann's Equation.	*Reststrahlen.*
Ag	215	220	211	—
Al	398	413	369	—
Ca	226	—	238	—
Cd	168	174	133	—
Cu	315	341	326	—
Fe	453	484	399	—
Hg	97	—	61	—
Na	172	—	191	—
Pb	88	75	89	—
Tl	96	—	89	—
Zn	235	—	211	—
NaCl	281	305	355	281
KCl	230	227	271	230
KBr	177	—	216	177
CaF_2	474	510	567	$\begin{cases}442\\635\end{cases}$
FeS_2	645	696	—	—

139. The Specific Heats of Gases.—Considerable attention has of late years been directed to the problem of accounting for the observed variation of the specific heats of gases with temperature. The problem is more complicated than that of finding an equation for the variation of specific heat of a monatomic solid for the molecules of a gas have, in addition to their energy of translation, energy due to rotation of the molecule as a whole and also energy of vibration of the constituent atoms. It is convenient to deal with the contributions made to the specific heat by translations, rotations and vibrations separately.

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* Schrödinger, *loc. cit.*, p. 476.

Except for the very lowest temperatures the translational kinetic energy has the equipartition value of $\frac{3}{2}kT$ per molecule even for the most complex molecules. Thus a gas of which the molecules possess only energy of translation will have energy of amount $\frac{3}{2}\boldsymbol{R}T$ per gram molecule and the specific heat will be $\frac{3}{2}\boldsymbol{R}$. This is the value shown by the monatomic gases such as helium and argon.

A diatomic molecule may be considered as consisting of two particles at a mean fixed distance apart, each atom being able to vibrate with respect to the other. For such vibrations the energy will be half kinetic and half potential, so again assuming the energy to have the equipartition value, the total will be $\boldsymbol{R}T$ per gram molecule and the contribution to the specific heat $\boldsymbol{R}$.

As regards the energy of rotation a diatomic molecule, such as we are considering, may be considered as free to rotate about any axis perpendicular to the line of centres—the reason for excluding rotations about the line of centres will appear later—giving two degrees of freedom. Associated with each of these degrees of freedom will be energy of amount $\frac{1}{2}\boldsymbol{R}T$ per gram molecule, according to the classical theory, and the contribution to the specific heat by the rotations will be $\boldsymbol{R}$.

The total specific heat of a diatomic molecule should therefore, according to the classical theory, be given by:

$$C_v = \tfrac{7}{2}\boldsymbol{R} = 6{\cdot}95 \text{ cals. deg.}^{-1}.$$

This value is not shown by any gas, and hence it must be concluded that the equipartition principle fails in this case. We are therefore led to consider the possibility that the quantum theory might provide a satisfactory explanation of the observed values of the specific heats of gases.

140. Quantum Theory of Specific Heats of Gases.—A detailed exposition of the quantum theory of specific heats of gases would lead us too far afield, but the explanation of some of the more important experimentally observed results may be indicated.

According to the quantum theory the energy of a rotating body is quantized according to the law:

$$I\omega = jh/2\pi,$$

where I is the moment of inertia, ω the angular velocity, h Planck's constant, j being able to adopt any of the values 1, 2, 3, etc. Consequently the rotational energy, E_j, is given by:

$$E_j = \tfrac{1}{2}I\omega^2 = j^2h^2/8\pi^2I.$$

The new quantum mechanics modifies this expression by replacing j^2 by $j(j + 1)$, when we have:

$$E_j = j\,(j + 1)\,h^2/8\pi^2I \quad . \quad . \quad . \quad . \quad (307)$$

It will be noticed that the minimum energy above zero possessed by a rotating molecule is inversely proportional to the moment of inertia. It is for this reason that rotations about the line of centres of a diatomic molecule are neglected, for the moment of inertia about this axis is so small that the minimum energy above zero is so large as to be possessed by very few molecules indeed.

It can be shown* that the statistical weight of a system with quantum number j is $(2j + 1)$, and using the distribution law we have previously employed, equation (290), it follows that the average energy per molecule due to rotations of the type considered is given by:

$$\bar{E} = \frac{\sum\limits_0^\infty (2j + 1)\,E_j e^{-E_j/kT}}{\sum\limits_0^\infty (2j + 1)\,e^{-E_j/kT}}$$

$$= -\frac{d}{d\mu}\log\,(2j + 1)\,e^{-\mu E_j}$$

where μ is written for $\dfrac{1}{kT}$.

The rotational specific heat is obtained by multiplying $\bar{E}$ by N, the number of molecules in a gram molecule, and differentiating with respect to T. If the substitution

$$\sigma = h^2/8\pi^2I\,kT$$

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* R. H. Fowler, *Statistical Mechanics.* This book contains a complete account of the whole theory.

is made, it is easily shown that the specific heat may be expressed in the form

$$C_v^{\text{rot.}} = \frac{d}{dT}(N\bar{E}) = \sigma^2 \boldsymbol{R} \frac{d}{d\sigma^2} \log \sum_0^\infty (2j+1)\, e^{-\sigma j(j+1)} \quad . \quad (308)$$

It can be shown that as T approaches zero so also does $C_v^{\text{rot.}}$, and also that the limiting value of $C_v^{\text{rot.}}$ for T large is $\boldsymbol{R}$.

The above theory has been used by Dennison* to account for the observed values of the specific heat of hydrogen. Equation (308) cannot be used directly as it stands since hydrogen exists in two forms, symmetrical and antisymmetrical, corresponding to j even and j odd, in the ratio 1 to 3. Consequently the measured specific heat corresponds to that of a mixture of different gases in this ratio the specific heat of each part being obtained by selecting the terms from equation (308) with j even for the symmetrical form and j odd for the antisymmetrical form. Using the value $4{\cdot}64 \times 10^{-41}$ c.g.s. for the moment of inertia of the hydrogen molecule, a value confirmed by the work of Hori† on band spectra, close agreement between theory and experiment is obtained.

For hydrogen $C_v^{\text{rot.}}$ is effectively equal to $\boldsymbol{R}$ above 300° K and to zero below 40° K. Since the above equation may be written

$$C_v^{\text{rot.}} = f(\sigma),$$

and I and T occur in σ only as the product IT, it follows that the temperature at which $C_v^{\text{rot.}}$ has an assigned value will be proportional to I^{-1}. That is the larger the value of I the lower the temperature at which $C_v^{\text{rot.}}$ becomes effectively equal to $\boldsymbol{R}$. Thus it is that observations of a variable $C_v^{\text{rot.}}$ are impracticable for all diatomic molecules which contain no hydrogen atom.

The vibrational energy of the diatomic molecule may be approximated to by supposing there to be a single vibrational frequency. The vibrational specific heat per gram molecule, $C_v^{\text{vib.}}$ will then be represented by Einstein's equation in the form:

$$C_v^{\text{vib.}} = \boldsymbol{R} \cdot \frac{x^2 e^x}{(e^x - 1)^2}$$

where x is written for $\dfrac{h\nu}{kT}$.

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[*] Dennison, *Proc. Roy. Soc. A.*, **115**, 483 (1927).

[†] Hori, *Zeit. f. Phys.*, **44**, 834 (1927).

Although this simple form will give a fairly accurate representation of the experimental results over considerable temperature ranges, a more accurate investigation is required when the results at high temperatures (up to 2,500° K) are considered. This has been provided, for example, by McCrea[*] in the case of hydrogen. McCrea started with the vibrational and rotational states of the normal hydrogen molecule as given by Hori[†] from an analysis of the band spectrum. From these results the average energy of a molecule due to vibrations and rotations was calculated in terms of T, and by differentiation the contribution made to the specific heat was found. The numerical values obtained in this way are in good agreement with those found experimentally.

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[*] McCrea, *Proc. Camb. Phil. Soc.*, **24**, 80 (1928).

[†] Hori, *loc. cit.*

APPENDIX I

SYSTEMS OF NOTATION

A JOINT Committee of the Chemical Society, Faraday Society and the Physical Society has recently issued a report on symbols for thermodynamical and physico-chemical quantities, and conventions relating to their use. These have been adopted as recommended practice in the publications of these societies, and should go far to standardize the notation in common use. It is undoubtedly to be desired that there should be some uniformity of practice in this matter, for when comparing different treatments of the same subject matter to have to remember three or four different notations occasions an extra mental strain, which adds to the difficulty of the subject, especially for beginners.

The recommended notation has been largely adopted in the text, and the following table gives a comparison, for some of the more important symbols, of those recommended and those adopted in the text.

	Recommended.	Text.
Heat	q	q
Work	w . . . W	W
Temperature, on absolute scale (°K) ..	T	T
Pressure	p, P	p (P)
Volume	v, V	v (V)
Entropy	S	S
Internal energy	U . . . E	E
Total heat	H	H
Thermodynamic potential at constant volume (Helmholtz free energy)	A	A
Thermodynamic potential at constant pressure (Gibbs' function)	G	G
Chemical potential	μ	μ
Mechanical equivalent of heat	$\boldsymbol{J}$	$\boldsymbol{J}$
Gas constant per gram molecule	$\boldsymbol{R}$	$\boldsymbol{R}$
Faraday's constant	$\boldsymbol{F}$	$\boldsymbol{F}$
Planck's constant	$\boldsymbol{h}$	$\boldsymbol{h}$
Boltzmann's constant	$\boldsymbol{k}$	$\boldsymbol{k}$

In the column headed Recommended, where two symbols separated by a comma are given for a quantity these symbols are to be regarded as alternatives for which no preference is expressed; where two symbols are separated by a dotted line the former is the first preference. In the column headed Text, symbols occasionally used for the same quantity are shown in brackets. The use of bold Roman type in the text has been restricted to denoting the properties of an arbitrary mass.

APPENDIX II

ADOPTED AND MOST PROBABLE VALUES FOR CERTAIN FUNDAMENTAL CONSTANTS

THERE is in existence no universally accepted list of the most probable values of the fundamental constants of physical science. Since numerical values of certain constants have to be used frequently in reducing experimental data, difficulty is often experienced in comparing the results obtained by one observer with those obtained by another, owing to the use of different numerical values for these constants. Such comparisons, and the recalculation of results as more exact information becomes available, would be greatly simplified if there existed an agreed list, periodically revised, of such numerical values.

Probably the most widely used collection of experimental data at the present day is that to be found in the International Critical Tables. For the purposes of the computations involved in the compilation of these tables, accepted values, or values which may be regarded as exactly correct for the purposes of computation, were adopted, and conversions and calculations made using these values. These are not necessarily the most accurate values that may be assigned at the present time, and an extremely important and comprehensive review by Birge* gives the most probable values of the constants according to information available when the review was written (1929-1932).

Since the International Critical Tables are so widely used the values of certain constants as adopted in that compilation and those found by Birge are given in the following table.

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* Birge, *Reviews of Modern Physics*, **1**, 1 (1929) and *Phys. Rev.*, **40**, 228 (1932).

	Units.	Value (I.C.T.).	Value (Birge).
Normal atmosphere	dyne cm.$^{-2}$	$1{\cdot}013250 \times 10^6$	$(1{\cdot}013249 \pm 0{\cdot}000003) \times 10^6$
Volume of one gram molecule of perfect gas at 0° C. and one normal atmosphere pressure	cm.^{3} mol^{-1}	$(22{\cdot}4115 \pm 0{\cdot}002) \times 10^3$	$(22{\cdot}4141 \pm 0{\cdot}0008) \times 10^3$
Gas constant per gram molecule ..	cal$_{15}$ deg.$^{-1}$ mol^{-1}	$1{\cdot}9869$	$1{\cdot}9864_8 \pm 0{\cdot}0004$
,, ,, ,, ,, ,, ..	erg deg.$^{-1}$ mol^{-1}	$8{\cdot}315 \times 10^7$	$(8{\cdot}3136 \pm 0{\cdot}0010) \times 10^7$
Temperature of melting ice on absolute scale..	°K	$273{\cdot}1$	$273{\cdot}18 \pm 0{\cdot}03$
Mechanical equivalent of heat ..	abs.-Joule cal$_{15}^{-1}$	$4{\cdot}185$	$4{\cdot}1852 \pm 0{\cdot}0006$
Electronic change	abs. e.s.u.	$(4{\cdot}774 \pm 0{\cdot}005) \times 10^{-10}$	$(4{\cdot}770 \pm 0{\cdot}005) \times 10^{-10}$
Faraday	abs. coulombs	$(9{\cdot}6500 \pm 0{\cdot}0010) \times 10^4$	$(9{\cdot}6489 \pm 0{\cdot}0007) \times 10^4$
Avogadro's number	mol^{-1}	$6{\cdot}061 \times 10^{23}$	$(6{\cdot}064_{36} \pm 0{\cdot}006) \times 10^{23}$
Planck's constant	erg sec.	$6{\cdot}554 \times 10^{-27}$	$(6{\cdot}547 \pm 0{\cdot}008) \times 10^{-27}$
Boltzmann's constant	erg deg.$^{-1}$	$1{\cdot}372 \times 10^{-16}$	$(1{\cdot}3708_9 \pm 0{\cdot}0014) \times 10^{-16}$
Acceleration of gravity (standard or normal)	cm. sec.$^{-2}$	$980{\cdot}665$	$980{\cdot}665$
Velocity of light	cm. sec.$^{-1}$	$(2{\cdot}9986 \pm 0{\cdot}0003) \times 10^{10}$	$(2{\cdot}99796 \pm 0{\cdot}00004) \times 10^{10}$

The ± sign in the column headed I.C.T. indicates what is there termed the uncertainty, and in the column headed Birge the probable error (according to the Gauss error law).

EXAMPLES

THE following values are assumed in the numerical examples:

Mechanical equivalent of heat = $4{\cdot}185 \times 10^7$ ergs/calorie.
Temperature of melting ice on the absolute scale = $273{\cdot}10^\circ$.
Density of mercury at 0° C. = 13·596 gms./cc.
Acceleration due to gravity = 981 cms./sec./sec.
Gas constant = 1·987 cals./gram molecule.

CHAPTER II

1. Given that the density of oxygen at N.T.P. is 1·4290 gms./litre find the gas constant per gram. What is it for a gram molecule ? Express this result in calories/degree also. Find the gas constant per gram molecule for hydrogen in the same units given the density at N.T.P. as 0·08987 gms./litre.

Answer : $2{\cdot}596 \times 10^6$ ergs/deg.; $8{\cdot}308 \times 10^7$ ergs/deg.; 1·985 cals./deg.; 1·989 cals./deg.

2. Air, initially at a temperature of 15° C., is allowed to expand adiabatically until its volume is doubled. What is its new temperature ? If the pressure was originally atmospheric, what would the final pressure be ? Take the ratio of the specific heats as 1·4.

Answer : $-54{\cdot}78^\circ$ C.; 0·3789 atmos.

3. Deduce an expression for the work done in the adiabatic expansion of a perfect gas in terms of temperature. If in the previous question the initial volume was 1000 ccs., what work would have been done ?

Answer : $\dfrac{R}{\gamma - 1}(\theta_1 - \theta_2)$ per gm.; $6{\cdot}136 \times 10^8$ ergs.

4. Find the work necessary to compress one litre of oxygen to one tenth of its volume the process being conducted isothermally at 0°C from an initial pressure of one atmosphere. What work would be done by the gas if it expanded adiabatically to its original volume ? Explain why these amounts of work are different. Take the ratio of the specific heats as 1·4.

Answer : $2{\cdot}334 \times 10^6$ ergs; $1{\cdot}525 \times 10^9$ ergs.

5. The behaviour of a certain fluid may be represented by the equation $\left(p + \frac{a}{v^2\theta}\right)(v - b) = R\theta$. Find the isothermal elasticity.

Answer: $$\frac{v \, . \, R\theta}{(v - b)^2} - \frac{2a}{v^2\theta}.$$

6. A vessel fitted with a wide stopcock is used to confine a gas at the same temperature as the atmosphere, and at a pressure p_1, which is greater than the atmospheric pressure P. The gas is allowed to expand adiabatically, by opening the stopcock momentarily, until its pressure falls to that of the atmosphere. The stopcock then being closed, the gas is allowed to regain its initial temperature when its pressure rises to p_2. Find an expression for the ratio of the specific heats in terms of p_1, P, p_2. (Clement and Desormes method).

Answer: $$\frac{\log p_1 - \log P}{\log p_1 - \log p_2}.$$

7. Show that for a fluid which obeys the equation $pv = R\theta$

$$v\left(\frac{dc_v}{dv}\right)_p = \theta\left(\frac{dc_v}{d\theta}\right)_p$$

and

$$p\left(\frac{dc_p}{dp}\right)_v = \theta\left(\frac{dc_p}{d\theta}\right)_v.$$

(*Note:* For a fluid obeying the given equation, $\left(\frac{dv}{d\theta}\right)_p = \frac{v}{\theta}$. The left-hand side of this equation may be expressed in terms of the variation in c_v.)

8. If δq is the small amount of heat absorbed by a substance in a certain process, show that it may be expressed in the form

$$\delta q = c_p\left(\frac{d\theta}{dv}\right)_p dv + c_v\left(\frac{d\theta}{dp}\right)_v dp.$$

Hence establish the relation

$$\left(\frac{d}{dv}\left\{c_v\left(\frac{d\theta}{dp}\right)_v\right\}\right)_p = \left(\frac{d}{dp}\left\{c_p\left(\frac{d\theta}{dv}\right)_p - p\right\}\right)_v.$$

(*Note:* Express dE in terms of dp and dv and substitute in the expression for the first law. Hence find the value of c_p, by making $dp = 0$. Remembering that $c_v = \left(\frac{dE}{dT}\right)_v$ the relation follows. The second relation follows from the condition that dE shall be a perfect differential.)

CHAPTER III

1. A perfect gas is made to go through a cycle consisting of two isothermal changes, at T_1 and T_2 respectively, and two changes at constant volume. If the volumes at the beginning and end of the isothermal expansion are v_1 and v_2, find an expression for the work done in the cycle. Assuming that the heat given out in one process at constant volume is stored in a regenerator and returned to the gas in the other constant volume process, find the efficiency of the cycle. (Stirling's cycle.) (Take $T_1 > T_2$; $v_2 > v_1$; c_v constant.)

Answer: $R(T_1 - T_2) \log \frac{v_1}{v_2}$ per unit mass; $\frac{T_1 - T_2}{T_1}$.

2. Prove that if the behaviour of a substance is represented by an equation of the type $p = Tf(v)$, the internal energy is independent of the volume. Show that the converse proposition is also true.

(*Note:* Express dE in terms of dT and dv; substitute in equation for dS and write down condition that this shall be a perfect differential.)

3. Show that the entropy of a perfect gas may be expressed in the form

$$S = c_p \log v + c_v \log p + C$$

if c_p and c_v are considered constant.

4. A substance is made to go through the following cycle of operations.

(i.) Heated at constant pressure from a temperature T_1 to T_2.
(ii.) Expanded adiabatically until its temperature falls to T_3.
(iii.) Cooled at a lower constant pressure until its temperature falls to T_4.
(iv.) Compressed adiabatically until its temperature again reaches T_1 and it has returned to its initial condition.

Assuming the specific heat to be constant and the same in each constant pressure process, obtain an expression for the work done in the cycle. If T_2 and T_4 are fixed, find the condition under which the work is a maximum. Evaluate the work under this condition.

Answer: $c_p(T_2 + T_4 - T_1 - T_3)$ per unit mass;
$T_1 = T_3 = \sqrt{T_2 T_4}$; $c_p(\sqrt{T_2} - \sqrt{T_4})^2$ per unit mass.

5. Two bodies of equal and constant thermal capacity c and at the absolute temperatures T_1 and T_2 are allowed to attain the same temperature T by the action of a reversible heat engine working between them. Find the value of T in terms of T_1 and T_2, and an expression for the external work done by the engine in the process.

Answer: $T = \sqrt{T_1 T_2}$; $c(\sqrt{T_1} - \sqrt{T_2})^2$.

6. If in the previous question the bodies had been allowed to attain the same temperature by being placed in direct thermal contact, what

would the loss of available energy have been ? Show that it is T_0 times the increase in entropy. Is there any loss of available energy in the previous method of equalizing the temperatures ? Explain the reasons for your answer.

Answer : $$cT_0 \log \frac{(T_1 + T_2)^2}{4T_1T_2}; \text{ No.}$$

7. A mass m_1 of a perfect gas at a pressure p_1 is allowed to mix with a mass m_2 of the same gas at a pressure p_2 without doing external work and in such a manner that the total volume occupied by the gas remains unchanged. Determine the increase in entropy. The mixing is supposed to take place in vessels impervious to heat.

Answer : $$R \log \left(\left\{ \frac{m_1p_2 + m_2p_1}{m_1 + m_2} \right\}^{m_1 + m_2} \cdot \frac{1}{p_1{}^{m_2}p_2{}^{m_1}} \right).$$

8. Calculate the increase of entropy which occurs when one litre of hydrogen at a pressure of one atmosphere mixes with one litre of hydrogen at three atmospheres pressure, the final volume occupied being 2 litres. The gas is all supposed to be at 0° C.

Answer : $$2{\cdot}459 \times 10^{-1} \text{ cal./deg.}$$

9. An absolute scale of temperature is defined in the following manner. The temperature of melting ice is taken as 0° and unit difference of temperature exists between two bodies when for a Carnot cycle working between them $\frac{W}{q} = \frac{1}{n}$. If θ is the temperature of a body on this scale find the relation between θ and T.

If $\frac{1}{n} = \frac{1}{3}$, what are the values of θ coresponding to the following values of T: 0°, 373·1°, 1000° ?

Answer : $$\theta = \log_{\frac{n}{n-1}} \frac{T}{273{\cdot}10}; \; -\infty; \quad 0{\cdot}768; \quad 3{\cdot}201.$$

10. A perfect gas expands in such a manner that its elasticity is always equal to the sum of the isothermal and adiabatic elasticities. Find its specific heat under these conditions in terms of that at constant pressure and at constant volume.

Answer : $$\frac{c_v{}^2}{c_p}.$$

CHAPTER IV

1. Establish a general equation for the difference between the specific heats at constant pressure for a substance subjected to pressures p_1 and p_2 at the same temperature.

Show that for a substance obeying the equation $\left(p + \frac{a}{v^2}\right)(v - b) = RT$ this difference is approximately $\frac{2a}{RT^2}(p_2 - p_1)$.

Answer : $$(c_p)_2 - (c_p)_1 = -T\int_{p_1}^{p_2}\left(\frac{d^2v}{dT^2}\right)_p dp.$$

2. Given that for carbon dioxide at N.T.P. the value of c_p is 0·200 cals./gm., use the results of the above example and the values of the constants in equation (94) to calculate the value of c_p at 50 and 100 atmospheres. Density of carbon dioxide at N.T.P. 1·9768 gms./litre.

Answer : 0·238 cals./gm.; 0·277 cals./gm.

3. Express equation (51) giving the variation of c_v with v in terms of the density ρ.

Answer : $$\left(\frac{dc_v}{d\rho}\right)_T = -\frac{T}{\rho^2}\left(\frac{d^2p}{dT^2}\right)_\rho.$$

4. Show that the difference of the isothermal and adiabatic compressibilities, β_T and β_S of any substance may be expressed in the form

$$\beta_T - \beta_S = \frac{Ta^2v}{c_p}$$

where a is the coefficient of volume expansion.

Find the percentage difference between these compressibilities in the case of water at 0° C. given the following data.

$c_p = 0{\cdot}9989$ cals./gm.; density $= 0{\cdot}9982$ gms./cc.;
$\beta_T = 45{\cdot}6 \times 10^{-12}$ dyne/cm.^{2}; $a = 5{\cdot}3 \times 10^{-5}/°$ C.

(*Note:* Write an expression for dv in terms of dT and dp. Hence find $\left(\frac{dv}{dp}\right)_S$ in terms of other differential coefficients. The equation can also be obtained from that for the difference between the specific heats of any substance by making use of the fact that the ratio c_p/c_v is the same as the ratio of the adiabatic and isothermal elasticities.)

Answer : 0·0404 per cent. of β_T.

5. Show that if the compressibility of a substance changes with temperature the coefficient of volume expansion changes with pressure. Explain the significance of this result in connection with experiments to determine the absolute coefficient of expansion of mercury (such as those of Regnault or Callendar and Moss).

Given the following values of the relative volumes of mercury at different pressures and temperatures, due to Bridgman, and assuming the coefficient of expansion of mercury at 0° C., 0·0001810, to be correct to four significant figures, at what pressure would its influence on the coefficient of expansion become of importance?

Pressure.	Temperature.	Volume.
0	0° C.	1·00000
0	20° C.	1·00362
10^6 gms./cm.^{2}	0° C.	0·99626
10^6 gms./cm.^{2}	20° C.	0·99972

Answer: $6{\cdot}25 \times 10^3$ gms./cm.^{2} or 6·05 atmos.

6. Obtain an expression, in terms of easily measurable quantities, for the change in temperature produced in a body when adiabatically compressed.

Find the change of temperature produced in a large mass of ether at 20° C. if the pressure is suddenly increased by ten atmospheres.

Density at 20° C. = 0·7135 gms./cc.; $c_p = 0{\cdot}56$ cals./gm. Coefficient of expansion = $1{\cdot}63 \times 10^{-3}$ per °C.

Answer: $dT = \frac{avT}{c_p} \cdot dp$, where a is the coefficient of expansion and dp the increase in pressure; 0·29° C.

7. Show that for a material in the form of a wire

$$\frac{1}{Y_T} - \frac{1}{Y_S} = \frac{a^2 T}{\rho c_p}$$

where Y_T and Y_S denote Young's modulus measured under isothermal and adiabatic conditions, a the coefficient of linear expansion, c_p the specific heat at constant tension, and T the absolute temperature.

Given the following values for steel at 0° C., find the percentage difference between Y_S and Y_T.

$a = 11{\cdot}0 \times 10^{-6}$ per °C.; $\rho = 7{\cdot}80$ gms./cc.;

$Y_T = 2{\cdot}00 \times 10^{12}$ dynes/cm.^{2}; $c_p = 0{\cdot}105$ cals./gm.

(*Note:* The work done by the system is no longer done by volume changes alone. If the stretching force is P, in an increase of length, dl, of the wire, work of amount Pdl is done *on* the system. Hence the expression for the first law takes the form $\delta q = dE - Pdl + pdv$. The term pdv will, in general, be very small compared with Pdl, and it is usual to neglect it. We may then write $\delta q = dE - Pdl$. Notice that the thermodynamic relations will now be different.)

Answer: 0·19 per cent.

8. A wire is stretched at a constant temperature T, and it is found that in order to maintain the temperature heat equivalent to the fraction $\frac{1}{n}$ of the work done in the extension has to be supplied. Find by how much the tension would vary if the temperature were to increase by one

degree and the length were maintained constant, the initial stretching force being P.

Answer: $$-\frac{P}{nT}.$$

9. From the following data calculate the change of entropy on heating one gram of mercury from — 270° C. to 0° C. at constant pressure.

Solid state:

Temp. °C.:	−270	−260	−240	−220	−200	−150	−100	−50	−40
$c_p \frac{\text{cals.}}{\text{gm.}} \times 10^2$:	0·026	0·549	2·02	2·53	2·81	3·07	3·21	3·31	3·33

Melting-point of solid = −38·7° C.; latent heat of fusion = 2·79 cals./gm.
Mean specific heat of liquid from melting-point to 0° C. = 0·0339 cals./gm.

Assuming that the entropy is zero at the absolute zero of temperature, and that for the lowest temperatures the specific heat varies as the cube of the absolute temperature (see Chapters IX and XIII), calculate the absolute entropy at 0° C.

(*Note:* Since the heating takes place at constant pressure $dS = \frac{c_p}{T}dT$.

Hence $$S_2 - S_1 = \int_{T_1}^{T_2} c_p d(\log T).$$

The simplest way of performing the integration is to plot c_p against $\log T$ on squared paper and integrate graphically. Often it is more convenient to plot $\log_{10} T$ and convert to Naperian logarithms after integration by multiplying by 2·30258.)

Answer: 0·0863 cals./deg.; 0·0864 cals./deg.

10. From the following data calculate the absolute entropy of one gram of argon at 0° C. and under one atmosphere pressure. Make the same assumptions as in the second part of the previous question.

Solid state	Temperature °K:	15	21	30	36	45	60	75
	c_p cals./gm. × 10:	0·38	0·88	1·13	1·37	1·48	1·65	1·88

Melting-point of solid = 83° K; latent heat of fusion = 6·71 cals./gm.
Mean specific heat of liquid = 0·264 cals./gm.
Boiling-point of liquid = 87° K; latent heat of vaporisation = 37·6 cals./gm.
Mean specific heat of gas from 87° K to 273·10° K = 0·129 cals./gm.

Answer: 0·919 cals./deg.

CHAPTER V

1. A fluid expands in such a manner that its internal energy remains constant. Find, for a small expansion, the ratio of the change of temperature of the fluid to its change of volume in terms of easily measurable quantities.

Answer:
$$\frac{p - T\left(\frac{dp}{dT}\right)_v}{c_v}.$$

2. Roebuck has found from a series of careful experiments that the product μc_p in the case of air at atmospheric pressure may be represented with sufficient accuracy by $\frac{A}{T} + B$, where A and B are constants. Find, by Buckingham's method, an expression for the ice melting-point temperature on the absolute scale. Evaluate this temperature from the following data.

Density of air at N.T.P. = $1{\cdot}293 \times 10^{-3}$ gms./cc.

Mean coefficient of expansion of air between 0° C. and 100° C. at a pressure of 100 cms. mercury = $3{\cdot}6730 \times 10^{-3}$ per °C.

Values of μc_p at atmospheric pressure.

Temperature	0° C.	100° C.
$\mu c_p \times 10^2$	6·404	3·216

c_p in cals./gm.; μ in °C./atmos.

The variation in μc_p between the pressures of 76 cms. and 100 cms. of mercury is negligible.

(*Note:* In evaluating the temperature the value of the density given above must be corrected to its value at the pressure at which a is measured. The correction obtained from the above data will be somewhat too high since, by taking the results for μc_p at 0° C. and 100° C. only, the values for intermediate temperatures are overestimated.)

Answer:
$$T_0 = \frac{1}{a} + \frac{1}{2av_0}\left\{\frac{646}{273 \times 373} \cdot A + 2B\right\}$$

where T_0 has been replaced by 273 in the correction term and A and B are expressed in terms of fundamental units; 273·18° K.

3. Using the equation $\mu c_p = \frac{A}{T} + B$ find by Buckingham's method a general expression for the corrections to be applied to the readings of a constant pressure air thermometer. When the gas scale temperature is 50° C. find the correction to convert this to the absolute scale. The pressure may be taken as 100 cms. of mercury. Use the data of Question 2.

Answer:
$$\frac{tA}{2v_0} \cdot \frac{1}{273}\left\{\frac{646}{373} - \frac{546 + t}{273 + t}\right\},$$

where t is the Centigrade temperature on the gas scale and A is in terms of fundamental units; $-0{\cdot}024°$.

4. Show that the correction to the ice-point on the constant pressure gas scale arrived at by Callendar's method, making use of the equation $\mu c_p = \frac{A}{T} + B$, is the same as that obtained by Buckingham's method if $\frac{p_0}{R}$ is replaced by $\frac{\theta_0}{v_0}$ and the approximation $273 = \theta_0 = T_0$ made elsewhere.

5. Given that $\mu c_p = \frac{A}{T} + B$, use Callendar's method to obtain a general expression for the correction to be applied to the ice-point on the constant volume gas scale to obtain the absolute melting-point of ice. Assume $T_0 = \theta_0 = 273$ in the correction term.

If the mean pressure coefficient, $\frac{1}{p_0}\left(\frac{dp}{dT}\right)_v$, for air at an initial pressure of 100·2 cms. of mercury between 0° C. and 100° C. is $3{\cdot}6744 \times 10^{-3}$, use the data of Question 2 to evaluate this temperature.

Answer : $\frac{A}{2v_0}$; 273·29° K.

6. Show that
$$-\left(\frac{d(\mu c_p)}{dT}\right)_p = \left(\frac{dc_p}{dp}\right)_T.$$

From the data given in Question 2 calculate the value of $\left(\frac{dc_p}{dp}\right)_T$ at N.T.P. and compare with the value obtained from the equation (due to Holborn and Jacob)
$$c_p \times 10^4 = 2413 + 2{\cdot}86\,p + 0{\cdot}0005\,p^2 - 0{\cdot}00001\,p^3,$$
where c_p is in cals./gm. and p in kg./cm.^{2}.

Answer : $4{\cdot}35 \times 10^{-4}$; $2{\cdot}96 \times 10^{-4}$. ($c_p$ in cals./gm.; coefficients per atmosphere.)

7. The " free expansion " or Joule coefficient may be defined by the equation $\eta = \left(\frac{dT}{dp}\right)_E$. Show that the connection between η and μ may be expressed in the form
$$\eta\left\{c_p - \left(\frac{d(pv)}{dT}\right)_p\right\} = c_p\mu + \left(\frac{d(pv)}{dp}\right)_T.$$

Given the data for μc_p in Question 2 and the following values, calculate η at 0° C. and 100° C. at one atmosphere pressure.

Temperature	$\left(\frac{d(pv)}{dp}\right)_T$	$\left(\frac{d(pv)}{dT}\right)_p$	c_p cals./gm.
0° C.	$-4{\cdot}33 \times 10^{-4}$	$2{\cdot}835 \times 10^{-3}$	0·2405
100° C.	$+0{\cdot}92 \times 10^{-4}$	$2{\cdot}835 \times 10^{-3}$	0·2424

In these data v is in litres/gm. and p in atmospheres. Express your answer in °C./atmos.

Answer: 0·312 °C./atmos.; 0·198 °C./atmos.

8. Show how from a knowledge of the manner in which μc_p varies with temperature and of the ice melting-point temperature the "cooling effect" equation may be made the basis of a method for finding how the mean coefficient of expansion of a gas between fixed temperatures varies with the pressure. Given the following data, and assuming $\mu c_p = \frac{A}{T} + B$, where A and B are constants, find this mean coefficient for air between 0° C. and 100° C. the pressure being 100 atmospheres.

μc_p at 100 Atmospheres.	Temperature.
$4{\cdot}997 \times 10^{-2}$	0° C.
$2{\cdot}359 \times 10^{-2}$	100° C.

μ is in °C./atmosphere and c_p in cals./gm.
Specific volume of air at 0° C. and 100 atmospheres = 7·49 cc.

Answer: $4{\cdot}403 \times 10^{-3}$/°C.

CHAPTER VI

1. Calculate the values of $\frac{RT_c}{p_c v_c}$ from the following data, and compare with the value given by Van der Waals' equation.

Substance.	Molecular Weight.	t_c °C.	p_c Atmos.	ρ_c gms./cc.
Helium ..	4·00	$-267{\cdot}9$	2·26	0·0693
Oxygen ..	32·00	$-118{\cdot}8$	49·7	0·430
Carbon dioxide	44·00	31·1	73·0	0·46
Ammonia ..	17·03	132·4	111·5	0·235

Answer: 3·33; 3·42; 3·57; 4·14.

2. Calculate the constants a and b of Van der Waals' equation in the case of helium from the data of Question 1.

At 0° C. it is found from experiment that the connection between p and v in the case of helium is given by

$$pv = 5{\cdot}5992 \times 10^3 + 2{\cdot}79\,p,$$

where the pressure is in atmospheres and the volume in ccs./gm. Using the values of a and b obtained from the critical data find the percentage error in the values of p given by Van der Waals' equation when the volume is 1·000, 0·050, and 0·010 of its volume under atmospheric pressure.

(*Note:* The poor agreement of the pressures from Van der Waals' equation with the experimental results, which would be worsened by the use of the value of **R** from the critical point data, illustrates that the method of obtaining the constants from the critical data is of little value. A much better agreement may be obtained by a suitable choice of the constants, but the simple relationships at the critical point are no longer valid.)

Answer: 4·81; $1·41 \times 10^8$; 0·08%; 0·63%; 3·21%.

3. The following are the experimental values for carbon dioxide at 0° C. under its saturation pressure.

Specific volume of liquid = 1·0811 cc./gm.
Specific volume of vapour = 10·26 cc./gm.
Saturation pressure = 34·379 atmos.

From these values calculate the value of the constant b in Van der Waals' equation and compare with that obtained from the critical data and that given in equation (94).

(*Note:* This method of procedure makes the equation an accurate representation of certain experimental results at the selected points—with the assumed value of **R**—but the general representation of all the experimental results will be much less accurate.

Two methods are available for finding b. Since p is the same for each of the given values of v, we have two equations in which the constants a and b are to be treated as the unknown quantities. Elimination of a results in a quadratic equation in b. A better method for finding b is that of successive approximations. In using the latter method substitute the approximate value of b in the term $(v_2 - b)$ where v_2 is the vapour volume. A guide to the approximate value of b is provided by the critical data.)

Answer: 0·795 cc./gm.

4. Show that the latent heat of vaporisation, l, of a liquid is given by the equation

$$l = T\int_{v_1}^{v_2}\left(\frac{dp}{dT}\right)_v dv$$

where v_1 and v_2 are the specific volumes of the liquid and vapour respectively.

From the data of the previous question calculate the latent heat of vaporisation of liquid carbon dioxide at 0° C. on the assumption that the behaviour of the fluid is represented by the equation of Van der Waals. Express your result in cals./gm. (Use the value of b from Question 3; the experimental result is 55 cals./gm.)

Answer: 43·2 cals./gm.

5. The pressure and volume of a fluid obeying the equation of Van der Waals were measured during adiabatic change and the apparent

ratio of the specific heats, γ', calculated from the relation $pv^{\gamma'} = \kappa$. Show that the true ratio of the specific heats, γ, is given approximately by:

$$\gamma = \gamma'\left(1 + \frac{a}{pv^2} - \frac{b}{v}\right).$$

(*Note:* From the assumed relation for reducing the experimental results, $\left(\frac{dp}{dv}\right)_s = -\gamma' \cdot \frac{p}{v}$. It is required to find an expression for $\left(\frac{dp}{dv}\right)_s$ in terms of γ and differential coefficients which may be found from Van der Waals' equation. Equating the two expressions for $\left(\frac{dp}{dv}\right)_s$ gives γ in terms of γ'.)

6. Brinkworth has measured the ratio of the specific heats of hydrogen by observing the pressure and temperature changes in adiabatic expansion. The value he obtains at 0° C., and one atmosphere pressure, by reducing his results according to the equation $T/p^{\frac{\gamma'-1}{\gamma'}} = \kappa$, is $1{\cdot}4098$. Assuming hydrogen to obey Berthelot's equation, find an expression for the true value. Show that this exact equation may be simplified by substitution from the equation $pv = RT$, and express the resulting equation in terms of the reduced pressure and temperature. Use the following critical data to find the true ratio of the specific heats of hydrogen.

$$T_c = 33{\cdot}2^\circ \text{ K}, \quad p_c = 12{\cdot}8 \text{ atmos.}$$

Answer: $$\gamma = \frac{\gamma'}{1 - (\gamma' - 1)\dfrac{2a}{Tpv^2}}; \quad \gamma \doteqdot \gamma'\left(1 + (\gamma' - 1)\frac{27}{32}\frac{\pi}{\tau^3}\right)$$

where π is the reduced pressure and τ the reduced temperature; $1{\cdot}4099$.

7. Using Dieterici's equation in the form

$$p = \frac{RT}{v - b}\, e^{-\frac{a}{RvT^{3/2}}}$$

find the reduced equation. Show that the value of $\frac{RT_c}{p_c v_c}$ is $3{\cdot}69$, and that this is more nearly the average experimental value than that given by Van der Waals' equation.

Answer: $$\pi = \frac{\tau}{(2\nu - 1)}\, e^{2\left(1 - \frac{1}{\nu\tau^{3/2}}\right)}$$

where π, τ and ν are the reduced pressure, temperature, and volume respectively.

8. Using Dieterici's equation in the form given in Question 7, find the condition for the inversion of the cooling effect and the equation to the locus of the points of inversion on the reduced temperature-pressure diagram.

Draw this locus and ascertain how well it represents the following inversion points for nitrogen experimentally determined by Roebuck.

Pressure Atmosphere.	Inversion Temperatures ° C.
20	330·0 — 167·0
100	277·2 — 156·5
220	212·5 — 117·2
300	158·7 — 68·7
360	93·7 — 10·0
376	40·0 + 40·0

$p_c = 33{\cdot}5$ atmos. $T_c = 126{\cdot}0°$ K.

(*Note:* The differentiations involved in this and the previous question are most easily accomplished by writing the originl equation in logarithmic form.)

Answer : $$\pi = \frac{10 - \tau^{3/2}}{\tau^{1/2}} e^{2\left(1{\cdot}2 - \frac{2}{\tau^{3/2}}\right)}$$

where π and τ are the reduced pressure and temperature. This equation gives the following values for π and τ at the maximum pressure for inversion: $\pi = 15{\cdot}328$, $\tau = 2{\cdot}5198$.

The experimental values are $\pi = 11{\cdot}22$ and $\tau = 2{\cdot}485$.

CHAPTER VII

1. Show, without the derivation or use of any formula, that for a substance which contracts on melting increase of pressure lowers the melting-point.

(*Note:* Draw a small Carnot cycle for the substance on a $p - v$ diagram. Consider taking the substance round this cycle, and remember that for external work to be done by the substance heat must be absorbed at the higher and rejected at the lower temperature.)

2. Show that in an infinitesimal change in a system of unit total mass consisting of two phases of the same substance in equilibrium with one another, the change of entropy may be expressed as

$$dS = \frac{l}{T} dm + \frac{(1 - m)s_1 + ms_2}{T} \,.\, dT,$$

where m is the mass existing in the second phase, s_1 and s_2 being the specific heats of the substance in the two phases.

Hence deduce the equations of Clapeyron and Clausius.

(*Note:* Since dS is a perfect differential, the application of the condition for a perfect differential to the above expression for dS gives the equation of Clausius. Clapeyron's equation may be obtained from the first term alone, i.e. $\left(\frac{dS}{dm}\right)_T$, by remembering that the change in total volume is given by $dv = (v_2 - v_1)\, dm$.)

3. Find the change of entropy when a mixture of liquid and saturated vapour having unit total mass and initially at a temperature T_1 with a mass m_1 of vapour is heated to a temperature T_2 and the conditions are changed so that there is now a mass m_2 of vapour.

Hence show that the condition for constant entropy of such a mixture is given by

$$\int s_1 \frac{dT}{T} + \frac{lm}{T} = \text{constant.}$$

Answer :
$$\int_{T_1}^{T_2} \frac{s_1 dT}{T} + \frac{l_2 m_2}{T_2} - \frac{l_1 m_1}{T_1}.$$

4. Given the following data, calculate the angle between the hoar-frost line and the steam line on the $p - T$ diagram. (Express pressures in mms. of mercury.)

Temperature of triple point = 0·0° C.
Specific volume of vapour = $2{\cdot}045 \times 10^5$ ccs.
Specific volume of liquid = 1·0001 ccs.
Specific volume of solid = 1·0907 ccs.
Latent heat of fusion = 79·7 cals./gm.
Latent heat of vaporisation = 594·3 cals./gm.

(*Note:* The temperature of the triple point of water is so nearly 0·0° C. that no appreciable error is caused by so taking it in this example.)

Answer : 2° 17′ approx.

5. Above 250° C. the variation of vapour pressure of mercury with temperature may be represented by the equation

$$\log_{10} p = 9{\cdot}9073 - 0{\cdot}62500 \log_{10} T - \frac{3276{\cdot}6}{T},$$

where p is in mms. of mercury.

Find an equation for the variation of latent heat of vaporisation with temperature and evaluate this at the normal boiling-point, 356·9° C. (The experimental value at this temperature is 67·9 ± 2·7 cals./gm.)

Answer : $l = 74{\cdot}74 - 6{\cdot}46 \times 10^{-3}\, T$ cals./gm.; 70·67 cals./gm.

6. The vapour pressure of acetone between 40° C. and 80° C. may be represented approximately by the equation

$$\log_{10} p = \frac{-1.609 \times 10^3}{T} + 7.765,$$

the pressure being in mms. of mercury.

Find the normal boiling-point.

If the density is given by

$$\rho = 0.81248 - 1.1142 \times 10^{-3}\, t - 0.315 \times 10^{-6}\, t^2,$$

t being the Centigrade temperature, find the difference between the specific heat of the liquid at constant pressure and that when it is constrained to move along the liquid-vapour boundary curve at its normal boiling-point.

Answer : 56·3° C.; 5.59×10^{-4} cals./gm.

7. Show that the following values of the vapour pressure of lead obtained by Egerton, can be represented by an equation of the type $\log p = A - \frac{B}{T}$.

Temperature °K.	Pressure Mms. of Mercury.
838·3	1.31×10^{-4}
868·0	3.04×10^{-4}
922·1	1.55×10^{-3}
978·6	6.07×10^{-3}
1045·5	2.59×10^{-2}

Evaluate the constants and obtain an approximate value for the latent heat of vaporisation.

Answer : $\log_{10} p = 8.00 - \frac{10^4}{T}$; 221 cals./gm.

CHAPTER VIII

1. Consider from first principles the conditions for equilibrium of two phases of the same substance.

2. Show that the chemical potentials μ_1, μ_2, etc., of the components of a system may be regarded as the partial thermodynamic potentials of the components.

Further, show that for a single phase of a system the variation of thermodynamic potential in a small change may be expressed in the form

$$dG = -\mathbf{S}dT + \mathbf{v}dp + \Sigma\mu_1\, d\mathbf{M}_1$$

the summation extending over all the components in the phase.

3. Prove, for a single phase of a system, that in any small variation

$$-\mathbf{S}dT + \mathbf{v}dp - \Sigma\mathbf{M}_1\, d\mu_1 = 0.$$

Use this relation to show that for a liquid phase in equilibrium with a vapour phase the pressure will be a maximum or minimum at a given temperature when the compositions of the phases are identical.

Similarly the temperature will be a maximum or minimum at constant pressure under the same conditions.

4. Considering one phase of a system only, show that the following relations are of general validity.

$$\begin{aligned} d\mathbf{E} &= Td\mathbf{S} - pd\mathbf{v} + \Sigma\mu_1 d\mathbf{M}_1 \\ d\mathbf{H} &= Td\mathbf{S} + \mathbf{v}dp + \Sigma\mu_1 d\mathbf{M}_1 \\ d\mathbf{A} &= -\mathbf{S}dT - pd\mathbf{v} + \Sigma\mu_1 d\mathbf{M}_1. \end{aligned}$$

Hence show that the chemical potentials may be written in the form

$$\mu_1 = \left(\frac{d\mathbf{E}}{d\mathbf{M}_1}\right)_{\mathbf{S}, \mathbf{v}, \mathbf{M}_2 \ldots \mathbf{M}_c} \qquad \text{etc.}$$

Obtain similar relations for the chemical potentials in terms of **H** and **A**.

Answer: $\mu_1 = \left(\frac{d\mathbf{H}}{d\mathbf{M}_1}\right)_{\mathbf{S}, p, \mathbf{M}_2 \ldots \mathbf{M}_c} = \left(\frac{d\mathbf{A}}{d\mathbf{M}_1}\right)_{T, \mathbf{v}, \mathbf{M}_2 \ldots \mathbf{M}_c}$, etc.

5. A system consists of several phases in equilibrium at a temperature T and pressure p. Obtain a generalized form of Clapeyron's equation which is applicable to the system.

Hence show that for a system consisting of a salt in contact with its saturated solution and the vapour of the pure solvent the latent heat of evaporation of unit mass of the solvent, l, is given by

$$l = T\frac{dp}{dT}(v_3 + cv_1 - (1 + c)v_2),$$

where v_1, v_2 and v_3 are the specific volumes of the salt, liquid and vapour phases respectively, and c is the concentration of the solution.

Further, find the form of this equation if v_1 and v_2 are small in comparison with v_3, and the vapour may be considered to obey the perfect gas law.

(*Note:* The solution remains saturated; consequently as much salt as goes out of solution appears in the solid state.)

Answer: $\left(\frac{d\mathbf{S}}{d\mathbf{v}}\right)_T = \left(\frac{dp}{dT}\right)_\mathbf{v}$; $l = RT^2\frac{d\log p}{dT}$.

6. Use the result of the preceding example to find the amount of heat absorbed when salt sufficient for saturation is dissolved in unit mass of solvent.

Assume the vapour to behave as a perfect gas.

(*Note:* From the preceding example l is the quantity of heat given out when unit mass of solvent vapour combines at constant pressure and temperature with the quantity of salt necessary to form a saturated solution. The process may be accomplished in an alternative manner by condensing unit mass of the vapour to liquid solvent and then dissolving the salt in the solvent. Since the final state reached is the same in each case, the difference between the heat absorbed and the work done by the system is the same, i.e. the change in internal energy. Hence by writing down the change in internal energy for the two paths an expression for λ the required heat of solution may be obtained.)

Answer : $\lambda = RT^2 \dfrac{d}{dT}\left(\log \dfrac{p_0}{p}\right)$, where p_0 is the saturation vapour pressure of the pure solvent and p that of the solution both at the temperature T.

7. For any one phase of a system of two components prove the following relations:

$$\left(\frac{d\mu_1}{d\mathbf{M}_2}\right)_{T,\,p,\,\mathbf{M}_1} = \left(\frac{d\mu_2}{d\mathbf{M}_1}\right)_{T,\,p,\,\mathbf{M}_2},$$

$$\mathbf{M}_1\left(\frac{d\mu_1}{d\mathbf{M}_1}\right)_{T,\,p,\,\mathbf{M}_2} = -\,\mathbf{M}_2\left(\frac{d\mu_2}{d\mathbf{M}_1}\right)_{T,\,p,\,\mathbf{M}_2},$$

$$\mathbf{M}_1\left(\frac{d\mu_1}{d\mathbf{M}_2}\right)_{T,\,p,\,\mathbf{M}_1} = -\,\mathbf{M}_2\left(\frac{d\mu_2}{d\mathbf{M}_2}\right)_{T,\,p,\,\mathbf{M}_1}.$$

Hence show that if $\mathbf{M}_1\left(\dfrac{d\mu_1}{d\mathbf{M}_2}\right)_{T,p,\mathbf{M}_1} = -\,B$, a constant, all the other partial differential coefficients may be expressed in terms of B and the masses $\mathbf{M}_1$ and $\mathbf{M}_2$.

8. Express the small variation in the chemical potential of a substance in terms of the variations of pressure and temperature and of the masses of the other components in the same phase.

Use the equation so obtained to discuss the equilibrium of a solution of a salt in contact with the vapour of the pure solvent. By a method similar to that outlined in Question 6, show that the differential heat of dilution, i.e. the heat evolved when unit mass of solvent is added to so large a quantity of solution that the concentration may be regarded as unchanged, is given by

$$\lambda_d = RT^2\,\frac{d\log p/p_0}{dT},$$

where p is the vapour pressure of the solution, p_0 that of the pure solvent, both at the temperature T, and the vapour is considered to behave as a perfect gas.

Answer : $d\mu_1 = -\,S_1dT + v_1dp + \Sigma\left(\dfrac{d\mu_1}{d\mathbf{M}_1}\right)d\mathbf{M}_1$,

where the partial differential coefficients are at constant pressure and temperature, and the other masses are held constant. S_1 and v_1 are the specific entropy and volume of the component considered.

CHAPTER IX

1. Nitric oxide dissociates according to the equation

$$-2NO + N_2 + O_2 = 0.$$

Starting with air consisting of 79·2 per cent. nitrogen and 20·8 per cent. oxygen it is found that at 1604° C. the percentage of nitric oxide is 0·42, and at 1760° C., 0·64. Assuming the heat of reaction to remain constant over this temperature range calculate its value. (Percentages are in terms of volume.)

Answer: $4{\cdot}13 \times 10^{-4}$ cals.

2. A mixture of nitrogen and oxygen in equal proportions by volume is heated to 1700° C. Calculate the percentage of nitrogen which is converted into nitric oxide.

Make use of the data given in the previous question.

Answer: $9{\cdot}28 \times 10^{-1}$ per cent.

3. Phosphorous pentachloride dissociates according to the equation

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

At 200° C. the specific gravity of the mixture, with respect to air, is 4·851, and at 250° C., 3·991.

Calculate the degree of dissociation at each of these temperatures and the heat of dissociation at constant pressure over the range 200–250° C.

The specific gravity of undissociated phosphorus pentachloride may be taken as 7·192.

Answer: 0·4826; 0·8019; $1{\cdot}814 \times 10^4$ cals.

4. Show that in the dissociation of a solid component

$$\frac{d \log K_p'}{dT} = \frac{\Delta H'}{RT^2}$$

where $\Delta H'$ includes the heat of vaporisation of the solid.

The equilibrium vapour pressure of ammonium chloride at 280° C. is 138 mm. of mercury, and at 300° C. is 252 mm. Assuming the vapour to be completely dissociated into ammonia and hydrochloric acid, find the heat of reaction.

Answer: $3{\cdot}793 \times 10^3$ cals.

5. In the dissociation of calcium carbonate into calcium oxide and carbon dioxide, the pressure of the carbon dioxide at equilibrium is 32·7 mm. of mercury at 711° C. and 70·0 mm. at 748° C. Calculate the heat of reaction over this temperature range.

Answer: $4{\cdot}107 \times 10^4$ cals.

6. Obtain an equation giving the connection between the heat of reaction at constant pressure, ΔH, and that at constant volume, ΔE, for reactions between perfect gases.

Answer: $\Delta H = \Delta E + \Sigma \nu_1 RT.$

7. Find the degree of dissociation of water vapour into hydrogen and oxygen at 1500° K and 0·1 atmosphere pressure given that at this temperature and one atmosphere pressure the degree of dissociation is $1{\cdot}97 \times 10^{-4}$.

Answer: $4{\cdot}24 \times 10^{-4}$.

CHAPTER X

1. Show that if the total thermodynamic potential of a solution can be expressed in the form

$$G = \Sigma n_1 \left\{ G_1 + RT \log C_1 \right\}$$

where G_1 is independent of the concentration, and any vapour may be considered as a perfect gas, then Henry's Law is applicable to each solute.

Show further that the law of mass action is applicable to reactions in the solution.

(*Note:* For the first part of this question consider the equilibrium of the solute in the solution and in the vapour phase. The chemical potentials in the two phases must be equal.)

2. By a method similar to that outlined for the previous question show that the vapour pressure of the solvent is equal to $p_0 c_0$, where p_0 is the vapour pressure of the pure solvent under the same conditions of temperature and total pressure and c_0 is the concentration of the solvent in terms of gram molecules. (Raoult's Law for ideal solutions.)

3. Show that the condition of osmotic equilibrium is the equality of chemical potentials of the common component of the two phases.

Hence deduce the expression for the osmotic pressure, P, of a solution in the form

$$P = \frac{RT}{V} \log \frac{n_1 + n_2}{n_1}$$

where n_1 is the number of gram molecules of solvent, n_2 that of solute, and V the volume occupied by one gram molecule of solvent, assumed independent of the pressure.

4. A fixed amount of solute is mixed with two different and immiscible liquids. Find the relation existing between the concentrations of the solutions so formed.

Answer: At constant temperature the ratio of the concentrations (expressed in gram molecules) is constant.

5. Obtain an expression showing how the concentration of a saturated solution depends upon the pressure applied to the system.

(*Note:* Consider the chemical potentials of the solid and the solute in solution. The result cannot be expected to apply to solutions of high concentration.)

Answer: $\left(\frac{d \log c_s}{dp}\right)_T = -\frac{\Delta \mathbf{v}}{RT}$, where $\Delta \mathbf{v}$ is the increase in volume of the whole system on dissolving one gram molecule of the solute.

6. By considering the chemical potentials of a pure liquid in equilibrium with its vapour obtain the expression for the change of vapour pressure p with the change in the pressure P applied to the liquid in the form

$$VdP = vdp,$$

where V and v are the specific volumes of the liquid and vapour respectively.

7. What important conclusion may be stated with regard to the work obtainable in a reversible isothermal cycle?

Apply this principle to obtain the connection between the vapour pressure and curvature of the liquid surface in the form

$$p_1 = p + \frac{p\rho}{\sigma} \log \frac{p_1}{p} + \frac{2\gamma}{r},$$

where p is the saturation vapour pressure over the plane liquid surface, p_1 that outside a concave liquid surface of radius r, γ the surface tension, σ the density of the vapour near the plane surface, and ρ the density of the liquid.

Answer: The work obtainable is zero.

8. Assuming pure water to consist of molecules H_2O and ions H^+ and OH^-, and that the concentrations of H^+ ion at 0° C. and 25° C. are $0{\cdot}37 \times 10^{-7}$ and $1{\cdot}10 \times 10^{-7}$ respectively, find the heat of ionisation of water.

Answer: $1{\cdot}41 \times 10^4$ cals. (Absorbed in ionisation of one gram molecule.)

CHAPTER XI

1. The E.M.F. of the Weston Normal Cell

$HgCd_{12\cdot5\%}/CdSO_4 \,.\, \frac{8}{3}\, H_2O$ (saturated solution)/$HgSO_4$ (paste)/Hg

is given by

$$X_t = 1{\cdot}01827 - 4{\cdot}06 \times 10^{-5}(t-20) - 9{\cdot}5 \times 10^{-7}(t-20)^2 + 10^{-8}(t-20)^3 \text{ volts.}$$

Find the heat of reaction in the cell at 15° C. Find also the ratio of the heat supplied from outside to the heat of reaction when the cell works at this temperature.

Answer: 47370 cals.; $-8{\cdot}51 \times 10^{-3}$.

2. In the cell

Zn amalgam (concentration c_1)/$Zn\ SO_4$ solution/Zn amalgam (concentration c_2)

the zinc in the amalgam may be considered as being in the atomic form if the concentrations are low. Calculate the E.M.F. of the cell (in volts) at 15° C. if the concentrations are 0·003366 and 0·00011305 respectively.

Answer: 0·04213 volts.

3. Show that if the E.M.F. of a cell is zero at some temperature T_0, then the heat of reaction ΔH_0 at this temperature is given by

$$\frac{\Delta H_0}{nF} = T_0 \frac{dX}{dT},$$

and the E.M.F. at any other temperature by

$$X = \frac{\Delta H_0}{nF}\left(\frac{T}{T_0} - 1\right).$$

4. Show that the electrical work obtainable from a reversible cell is equal to the decrease in total thermodynamic potential. Hence obtain an equation for the E.M.F. of a concentration gas cell.

5. In the cell

Hg (liquid)/$Hg\ Cl$ (saturated solution)/Cl_2 (gas pressure p)

the reaction which takes place is

$$2Hg \text{ (liquid)} + Cl_2 \text{ (pressure } p) = 2HgCl \text{ (solid)}.$$

If the E.M.F. with a gas pressure of 0·0490 atmosphere is 1·0508 volts at 25° C. what would it be if the gas pressure were 0·010 atmosphere ?

Answer: 1·0304 volts.

6. Show that if the reacting substances in a cell are all in dilute solution, or may be considered as perfect gases, the E.M.F. of the cell is given by the equation

$$X = \frac{RT}{nF} \log K_c - \frac{RT}{nF} \Sigma \nu_1 \log c_1,$$

where K_c is the reaction constant under the given conditions, c_1 etc. the concentrations of the reactants, and n the number of Faraday's necessary for the reaction.

(*Note:* Make use of the fact that the electrical work obtainable from a reversible cell is equal to the decrease in thermodynamic potential, and express this in terms of the relations previously obtained for the thermodynamic potentials per gram molecule (chemical potentials) in dilute solutions or for perfect gases.)

7. Obtain the E.M.F. of a gas cell in terms of the reaction constant K_p. Given that the E.M.F. of the cell

H_2 (atmospheric pressure)/H_2SO_4 (dilute solution)/O_2 (atmospheric pressure)

is 1·236 volts at 18° C., calculate the degree of dissociation of saturated water vapour into oxygen and hydrogen at this temperature if the saturation vapour pressure is 15·46 mm. of mercury.

(*Note:* In practice this cell does not give such a high voltage as 1·236. This has been traced to the irreversibility of the oxygen electrode.)

Answer: $X = \frac{RT}{nF}\left\{\log K_p - \Sigma \log p_1^{\nu_1}\right\}$ where n is the number of Faraday's necessary for the reaction; $1·82 \times 10^{-27}$.

CHAPTER XII

1. The radiation from the sun received on the earth is approximately 2 calories per minute on one square centimetre perpendicular to the direction of the sun's rays. What pressure would this produce (*a*) on a black body on which it fell normally, (*b*) on a perfect reflector under the same conditions?

Assuming in case (*a*) that the energy is all re-radiated from the surface on which it falls initially what would be the pressure?

Answer: $4·65 \times 10^{-5}$; $9·30 \times 10^{-5}$; $7·75 \times 10^{-5}$. Each in dynes/cm.^{2}.

2. Using the data given in the above question find the approximate temperature of the sun and the wavelength corresponding to maximum energy density.

Take $\sigma = 5·7 \times 10^{-5}$ ergs sec.$^{-1}$ cm.$^{-2}$ deg.$^{-4}$.

Radius of earth's orbit $= 1·495 \times 10^{13}$ cms.
Radius of sun $= 6·96 \times 10^{10}$ cms.

Answer: 5800° K approx.; $4·97 \times 10^{-5}$ cms.

3. Find the form of the Stefan-Boltzmann law if the pressure exerted by radiation is n times the energy density. Deduce the form of Wien's general law in this case.

Answer: $E\ a\ T^{\frac{n+1}{n}}$; $E_\lambda = \frac{1}{\lambda^{3n+4}} F(\lambda^{3n} T)$.

CHAPTER XIII

1. Show that the Debye equation may be expressed in the form

$$\frac{C_v}{3R} = \frac{4\pi^4}{5x^3} - \frac{3x}{e^x - 1} - 12x \sum_1^\infty e^{-nx}\left(\frac{1}{nx} + \frac{3}{n^2x^2} + \frac{6}{n^3x^3} + \frac{6}{n^4x^4}\right)$$

where $x = \frac{h\nu_m}{kT}$ and n takes the values unity to infinity successively.

(*Note:* the integral $\int_0^x \frac{x^3}{e^x - 1}\,dx$ may be written $\int_0^x x^3(e^{-x} + e^{-2x} + \ldots)\,dx$, which may be integrated by parts term by term.)

2. Assuming $\frac{h\ {}_m}{k}$ for lead to be 94, use the result of the previous question to calculate the specific heat at 50° K to three significant figures.

Compare with the value obtained by linear interpolation from Table XVIII.

Answer: 5·03 cals./gm. atom; from Table XVIII 5·00 cals./gm. atom.

3. Taking the value of $\frac{h\nu}{k}$ for silver to be 157, calculate the value of C_v at 100° K from Einstein's equation to three significant figures.

Answer: 4·87 cals./gm. atom.

4. The melting-point of zinc is 419·4° C. The experimental values for C_p at 100° K and 200° K are 4·73 and 5·75 cals./gm. atom respectively. Calculate the difference between C_p and C_v at 100° K and 200° K.

Answer: 0·07 cals./gm. atom; 0·20 cals./gm. atom.

5. The relation between C_p and C_v for solid bodies can be approximately expressed by a relation, due to Magnus and Lindemann, in the form

$$C_p = C_v + aT^{5/2}.$$

Assuming this relation to be valid, and that the specific heat of the vapour does not vary with temperature, obtain an expression for the vapour pressure of a metal if the specific heat of the solid may be represented by Einstein's equation.

(*Note:* Make use of equation (144).)

Ans. $\log_e p = \frac{-L_0}{RT} + \frac{C_p}{R} \log_e T - \frac{4}{15} aT^{3/2} - 3x + 3 \log_e (e_x - 1) + i'$

where C_p is the specific heat of the vapour and $x = \frac{h\nu}{kT}$ or

$$\log_{10} p = \frac{-L_0}{4{\cdot}5754\, T} + \frac{C_p}{1{\cdot}987} \log_{10} T - 0{\cdot}0583\, aT^{3/2} - 1{\cdot}3029\, x + 3 \log_{10} (e^x - 1) + C,$$

where p is expressed in atmospheres.

6. Given the following data for cadmium, calculate the chemical constant using the result of the former question. (For logs. to base 10 and pressures in atmospheres.)

Atomic weight 112·4.

Temperature of melting-point 594° K.
Density 8·6 gms./cc.
Coefficients of linear expansion $28{\cdot}8 \times 10^{-6}$/°C. } At 291° K.
Compressibility $2{\cdot}22 \times 10^{-12}$ c.g.s.
Specific heat of vapour 4·963 cals./°C.

$$\log_{10} p \text{ at } 471{\cdot}8° \text{ K} = -3{\cdot}546$$
$$\log_{10} p \text{ at } 532{\cdot}5° \text{ K} = -2{\cdot}118$$

where p is expressed in mms. of mercury.

Take $\frac{h}{k} = 4{\cdot}78 \times 10^{-11}$.

(*Note:* First find the characteristic frequency by making use of Lindemann's melting-point equation.

By equating $aT^{3/2}$ to the thermodynamic expression for the difference of the specific heats a may be found.

Substitution of the two values for $\log_{10} p$ gives two equations between which L_0 can be eliminated. Remember that pressures are to be expressed in atmospheres.)

Answer : 1·38. This is lower than the true value for cadmium, about 1·45 to 1·57 from experiment. This is largely due to the method adopted above for finding ν and the use of Einstein's equation for the variation of specific heat with temperature.

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